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LEACHING OF OIL SHALE SOLID WASTES: A CRITICAL REVIEW

by

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CONTENTS

ABBREVIATIONS

bcy	billion cubic yards
BLM	Bureau of Land Management
BPD	barrels per day
COD	chemical oxygen demand
CSU	Colorado State University
DDP	detailed development plan
DEI	Development Engineering, Inc.
DOC	dissolved organic carbon
DOE	Department of Energy
DRI	Denver Research Institute
EC	electrical conductivity
EDC	Energy Development Consultants
EIS	environmental impact statement
EPA	Environmental Protection Agency
GC-IR	gas chromatography-infrared spectrometry
GC-MS	gas chromatography-mass spectrometry
HPLC	high performance liquid chromatography
IR	infrared spectrometry
LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory
LETC	Laramie Energy Technology Center
LLNL	Lawrence Livermore National Laboratory
MS	mass spectrometry
NAS	National Academy of Sciences
NBS	National Bureau of Standards
OTA	Office of Technology Assessment
pcf	pounds per cubic foot
PNL	Battelle Pacific Northwest Laboratory
R	liquid-to-solid ratio
T	tons
TDS	total dissolved solids
THF	tetrahydrofuran
TPD	tons per day
USDI	U.S. Department of Interior
VMIS	vertical modified in-situ retorting
XRD	x-ray diffraction

Chapter 1

INTRODUCTION AND SUMMARY

INTRODUCTION

The last decade has witnessed an explosion in research on the leaching of solids associated with shale oil production. Federal and state agencies and industry have sponsored millions of dollars in research in this area at private and public institutions. The leaching properties of many samples of raw and spent shales of widely differing histories have been examined using techniques ranging from simple batch tests, to exhaustive Soxhlet extractions, to long-term field studies. This has produced, not suprisingly, a diversity of opinions regarding the composition of leachates and their environmental significance.

The U.S. Department of Energy, through the Oil Shale Task Force, requested that this information be reviewed and evaluated to help direct and guide its future leaching research program. In particular, it was requested that attention be focused on (i) the diversity of techniques that have been used for leaching studies and (ii) an evaluation of the need for standardized techniques.

This report addresses these needs. It is a review and critical evaluation of the published research on the leaching of raw shale, surface spent shale, and in situ spent shale. A preliminary program for future leaching studies also is presented. Because much of the reviewed research has not been published in archival, refereed journals and is difficult to acquire, this report uses a wealth of figures and tables to present and discuss the data. It is hoped that this document will help facilitate discussion on leaching research needs and that consensus on future directions of the program will emerge and replace or modify the preliminary program proposed here.

This study is presented in six major chapters as follows:

- Chapter 1: Introduction and Summary
- Chapter 2: Retorting Technology
- Chapter 3: Raw Shale
- Chapter 4: Surface Spent Shale
- Chapter 5: In Situ Spent Shale
- Chapter 6: Leaching Plan

The first chapter summarizes the principal results and conclusions of the study. This is followed, in Chapter 2, by a discussion of surface and in situ retorting technology that was being considered for commercialization as of November 1981. This technology information is later used to relate leaching behavior and spent shale mineralogy to retort operating conditions. The next three chapters review leaching studies on raw shale, surface spent shale, and in situ spent shale, respectively. Each of these three chapters presents an engineering perspective on disposal procedures and reviews and evaluates available data on mineralogy, leachate characterization, leaching mechanisms, and leachate transport and effects. This review forms the basis of the leaching plan, in Chapter 6, which presents recommendations for future research on raw shale and spent shales.

SUMMARY

Large quantities of raw and spent shale will require temporary or permanent disposal at an oil shale plant. Solids from aboveground retorting will be stockpiled at the surface where they may be leached by rainfall and snowmelt, or they may be backfilled into the mine, where they may be leached by groundwaters (Figure 1-1). In the in situ processes, large chambers of spent shale and allied mining and processing works are left underground where they may be leached by groundwaters or precipitation. In the modified in situ process, raw shale mined to create void space will be stored on the surface. In near-surface, true in situ processes, precipitation may pass through the overburden and leach abandoned, underground retorts (Figure 1-2).

These types of impacts have been investigated in laboratory, field, and modeling studies for the past decade. The emphasis of this work has been on surface spent shale leachates. Comparatively little research has been conducted on the leaching of raw shales and of in situ spent shales. Interestingly, recent biological effects studies indicate that raw shale leachates may be more toxic to aquatic organisms than spent shale leachates. Also, chemical characterization studies reveal that raw shale leachates contain very high concentrations of organic carbon, NO_3, F, B, and other toxic trace elements; in many cases, these constituents occur at higher concentrations in raw shale leachates than in spent shale leachates. This is noteworthy since raw shale leachates have long been considered to be environmentally benign, and no special controls are planned at development sites to prevent deep percolation.

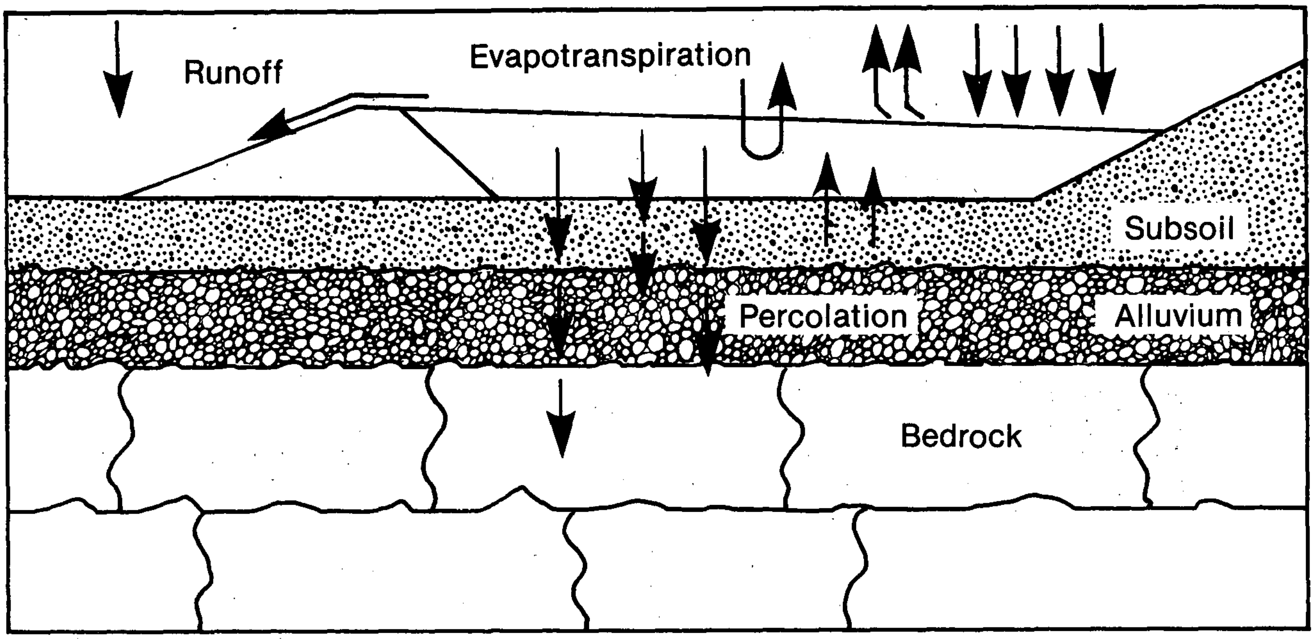
This section first presents the recommended leaching plan, which consists of six general recommendations and several specific recommendations. It then overviews the research that has been conducted on raw shale, surface spent shale, and in situ spent shale leachates.

Leaching Plan

The leaching plan consists of six general recommendations which apply to all types of leaching studies and certain additional, solid-waste-specific recommendations. The general recommendations address approaches to and management of leaching research while the specific recommendations focus on topics that require additional study or which have been omitted from the on-going program.

Six modifications and/or additions to the existing program are recommended. Some of these are in progress, and these existing programs should be fostered and accelerated. The six general recommendations are:

Surface Disposal Pile



Mine Backfill

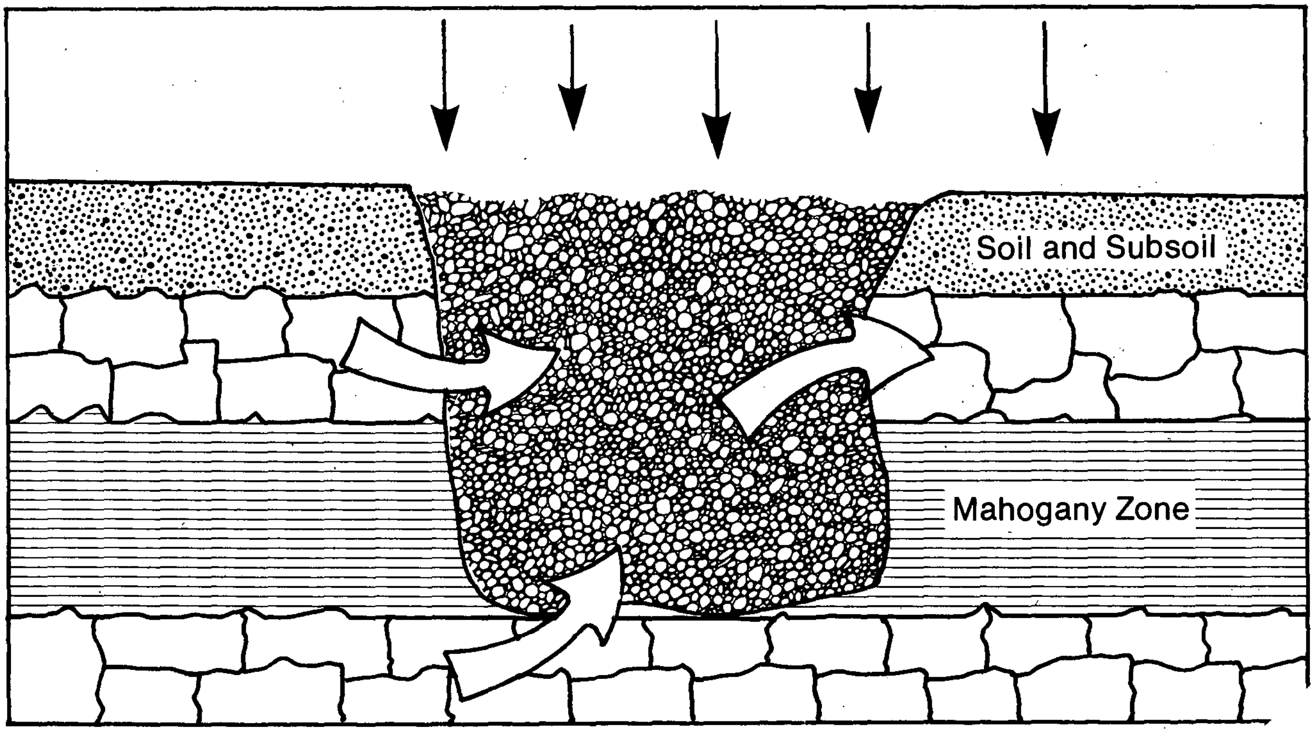
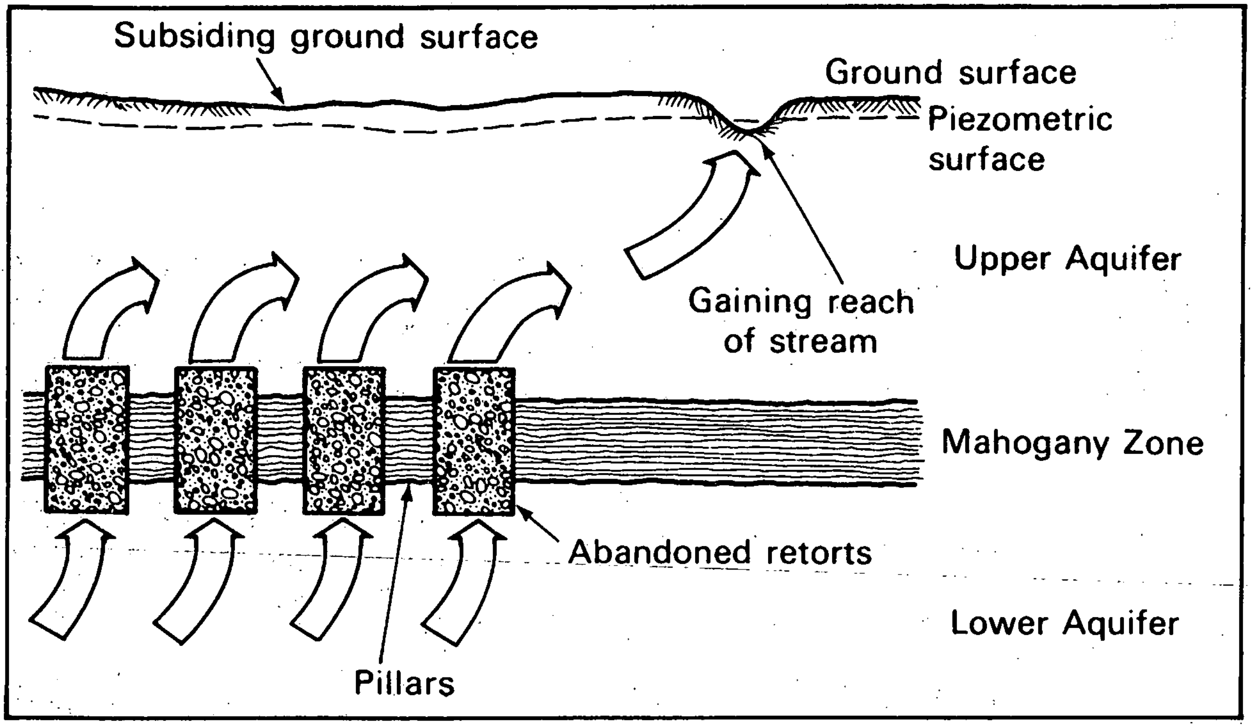


Figure 1-1. Schematic representation of potential impacts from surface and underground disposal of spent shale.

Modified In-situ Abandoned Retort (Based on Occidental Process)



Horizonatal True In-situ Abandoned Retort (Based on Geokinetics Process)

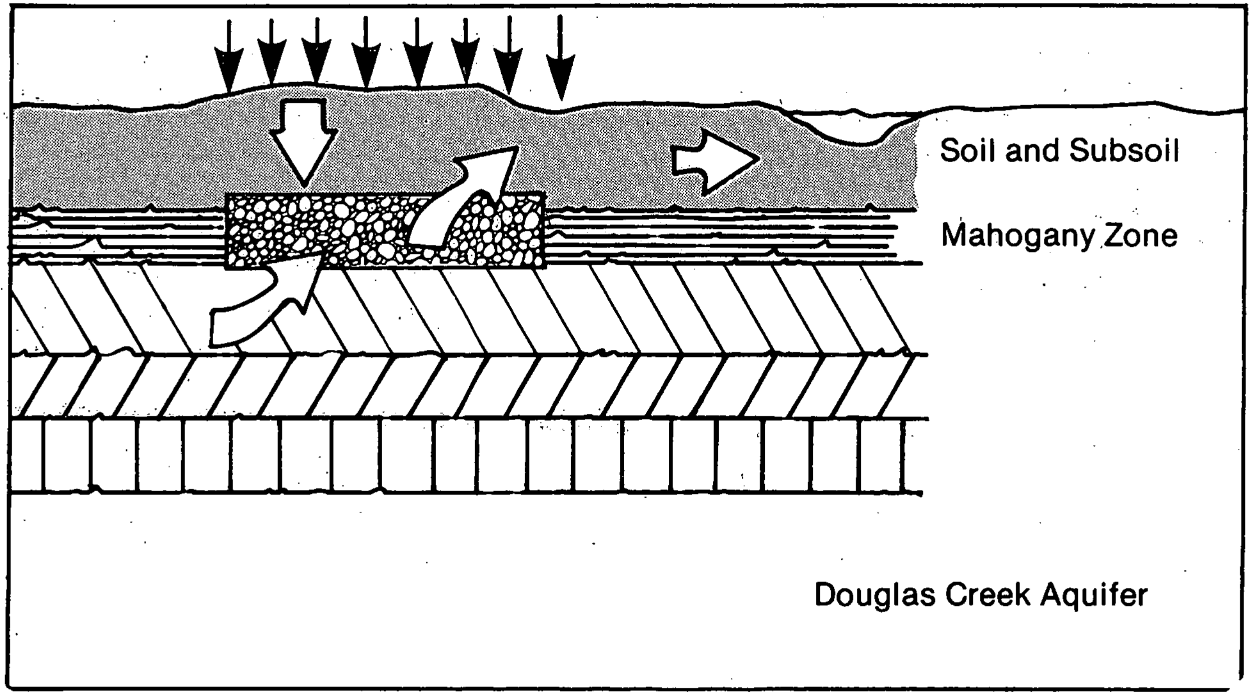


Figure 1-2. Schematic representation of potential impacts from modified in situ and near-surface horizontal, true in situ retorting.

- Geochemical and mass-transfer models should be developed for raw, surface, and in situ leachates and used to integrate existing information into a coherent theoretical framework and to help identify additional information requirements.

- A systems approach, which elucidates the interrelationship among raw shale, processing parameters, spent shale, and leachates, should be adopted.

- Future leaching studies should focus on samples from small laboratory reactors which are generated under carefully controlled and well-defined conditions, and research should be largely decoupled from industry plans. (Limited characterization studies using samples from near-commercial processes are also important to test laboratory models, for environmental assessments, and for permitting purposes. These are included in the discussion on specific recommendations.)

- The available data should be analyzed to determine environmental effects and risks of leachates to help focus the program on key issues.

- A standard leaching protocol and standard samples should be developed and used to calibrate and validate leachate results.

- Better coordination among agencies which fund oil shale research is required, and funding officers should encourage investigators to publish results in refereed and archival journals, rather than in obscure progress reports.

The specific research recommendations are summarized in Table 1-1. Those that should receive top priority in future programs are indicated by an asterisk (*). These recommendations have been divided into five categories for convenience: samples, characterization, field conditions, mechanisms, and simulations. Solid wastes which have not been studied and which appear important based on this review are listed under "samples." Chemical species or compound classes which have not been measured and are likely to be important are listed uner "characterization". Disposal conditions which will exist in the field and are likely to influence the quality of leachate, but which have been overlooked in experimental studies, are listed under "field conditions". It is recommended that these topics be explored under carefully controlled conditions in the laboratory. The environmentally important chemical species and the type of data required to predict their leaching and transport behavior are indicated under "mechanisms". The disposal conditions that should be studied with computer models and simulated in experimental studies are listed under "simulations".

Raw Shale Leachates

The leachate from each raw shale is unique, and it is difficult to make generalizations about raw shale leachates. This is likely due to differences in mineralogy which are presently poorly understood. Available data indicate that most raw shale leachates have a pH between 6 and 8 with some samples

TABLE 1-1

Summary of Specific Research Recommendations on Raw Shale, Surface Spent Shale, and In Situ Spent Shale Leachates.

Leachate From:	Samples	Characterization	Field Conditions	Mechanisms	Simulations
Raw Shale	• Feedstocks for Superior, Union, Chevron sites in Colorado • Feedstocks for proposed development sites in Utah • Subore, overburden, and fines from proposed developments	* Chemical speciation of inorganics, organics, and organometallics	• Leach water quality (e.g. acid rain)	• Release and transport of pH, TOC, TDS, NO_3, B, Mo, Li, Zn, As, Mn, S, Eh * Thermodynamic, kinetic, and hydrologic data for important physical, chemical, and biological processes (e.g., adsorption, precipitation) • Stoichiometry and kinetics of rock-water and aqueous-phase reactions	• Coarse-ore stockpile • Fines-reject pile • Subore and overburden storage
Surface Spent Shale	• Lurgi, Chevron, Union, Superior • Codisposed solids • Improved sample history documentation • Consistent comparison of different spent shales	* Chemical speciation of inorganics, organics, and organometallics	• Codisposal/volatilization • Revegetation • Catchment dam * Construction sequencing • Post-abandonment • Leach water quality (e.g., acid rain) • Field validation of laboratory procedures	• Release and transport of pH, TDS, S, F, B, Mo, Li, Eh * Thermodynamic, kinetic, and hydrologic data for important physical, chemical, and biological processes for leaching and leachate transport • Stoichiometry and kinetics of rock-water and aqueous-phase reactions	• Cross-valley fill, side-hill fill, and surface pile • Surface pile • Backfilled mine • Pile construction * Water movement • Effect of pile on natural recharge
In Situ Spent Shale		* Chemical speciation of inorganics, organics, and organometallics	• Retort cooling (gas, water) • Spent shale temperature • Unground sump, bottom plug • Post-retorting reactions between pillars and hot spent shale • More realistic field simulations * Leach water quality	• Release, transport, and control of pH, TDS, S, V, Pb, Se, Eh * Thermodynamic, kinetics, and hydrologic data for important physical, chemical, and biological processes for leaching and leachate transport	• Grouting • Intentional leaching * Fracture porosity

Notes: * = top priority

reaching higher values. The dissolved solids range from 100 to 10,000 mg/L with lower values occurring after several pore volumes of leachate have passed through a column. The major cations are Ca, Mg, Na, and K, and the major anions are SO_4, HCO_3, and Cl. Leachates from many samples of raw shale have elevated concentrations of organic carbon, NO_3, F, and B. Since raw shale piles are quite permeable, percolates from raw shale may pose a greater threat to groundwater quality than spent shale percolates.

Leaching characteristics of only a few samples of raw shale have been investigated. Most published work consists of preliminary screening tests (McWhorter, 1980; Jackson et al., 1975) or limited measurements made in conjunction with spent shale leaching or other types of studies (Margheim, 1975; Stollenwerk, 1980; Saether, 1980; Cleave et al., 1979). Investigations have been conducted on the effect of wetting and drying cycles and contact time on pH and on the concentrations of TDS, F, Mo, B, As, and Se in leachates (Stollenwerk, 1980; Saether, 1980; McWhorter, 1980). Other studies have investigated the effect of saturated and unsaturated conditions on leachate composition (McWhorter, 1980). Chemical species of F, B, Mo, and As have been determined in leachates using equilibrium models (Saether, 1980; Stollenwerk, 1980) or experimental techniques (Fox, 1982a). The release mechanisms and aqueous chemistry of F have been exhaustively studied for raw shale from the Colony Mine (Saether, 1980). Other work is in progress to evaluate the effect of raw shale mineralogy on leachate composition (Peterson, 1981) and to investigate raw shale leaching under field conditions (McWhorter, 1981b; Wildung et al., 1981).

Surface Spent Shale Leachates

Research has focused on surface disposal piles (no work has been conducted on backfilled mines) and on percolation. This work reveals that there are major differences in the chemical composition of runoff and percolation and among leachates from various surface retorting processes. The concentrations of most dissolved substances in both runoff and percolation decrease to low levels. However, if the samples are drained or dried and releached, the concentration of many ions returns to near initial levels. Percolates, on the other hand, have much higher initial and long-term concentrations of most dissolved substances, and percolation concentrations are slower to decrease. The initial high concentrations are attributed to rinsing of soluble salts from the surface of spent shale while the lower concentrations are attributed to mineral dissolution and slow diffusion of salts from micropores.

There are significant differences in the major and minor element concentrations among leachates from different spent shales (i.e., Paraho, TOSCO). These differences are generally consistent with spent shale mineralogy. Leachates have a pH that ranges from 8 for samples from low-temperature, indirect-mode processes up to 12 for samples from high-temperature, direct-mode processes. Field pHs may drop to 3 to 7 due to oxidation of S_2O_3 (Metcalf and Eddy, 1975; Garland et al., 1979; Stollenwerk, 1980). As noted for raw shale leachates, the major cations are Ca, Mg, Na, and K, and the major anions are SO_4, HCO_3, and Cl. Fluoride, B, and Mo are elevated in most surface spent shale leachates. Other elements, including Li, Si, and V, have been found at high levels in leachates from some samples. The highest concentrations of organics, which are largely polar with some polycyclic aromatic hydrocarbons, occur in leachates of spent shales from low-temperature, indirect-mode processes. Carbonate and sulfur chemistry of these leachates are important and control/dominate solution chemistry, pH, and redox state.

Field and transport studies reveal that soils and other geologic materials may retard the migration of many leachate solutes, including F, As, and Al. Exceptions include Cl, Li, SO_4, B, and alkylpyridines, which are mobile in the natural hydrologic system. Spent shale piles will probably be colonized by bacteria and fungi, and laboratory studies suggest that microbes may volatilize As (Klein et al., 1981) and oxidize S_2O_3 (Stollenwerk, 1980; Brierley and Brierley, 1981).

The majority of research on surface spent shales has used samples from the Paraho and TOSCO II processes. Laboratory and field studies have been used to develop characterization data; a mechanistic understanding of fundamental physical, chemical, and biological processes; and computer models that can be used to simulate leachate quality, production, and transport.

Accurate characterizations of leachates have been hampered by lack of representative spent shale samples, absence of actual disposal sites, and the difficulty of using simple laboratory tests to simulate the complex natural environment. The best characterization data has come from field studies (Wildung et al., 1980 - 1982; Garland et al. 1979, 1981; Harbert et al., 1979; Kilkelly et al., 1981; Harbert and Berg, 1978). Laboratory methods do not reliably simulate field conditions, and most laboratory studies have had other goals. Many have focused on developing a mechanistic understanding of the leaching process (Stollenwerk, 1980; Saether, 1980; Silviera et al., 1978; Runnells and Esmaili, 1981), on developing the analytical methods that will be used to characterize leachates or on qualitative organic characterizations (Schmidt-Collerus, 1976; Bonomo, 1974; Prien et al., 1977; Carpenter, 1978; Maase, 1980; Fox, 1982a).

Mechanistic studies have addressed leaching processes that occur in the immediate vicinity of a particle of spent shale and during subsequent transport. Culbertson et al. (1970), Farris (1979), and Taylor et al. (1982) have investigated the effect on leachate quality of retorting temperature and atmosphere. Others have addressed the effect of various thermodynamic, kinetic, hydraulic, and physical leaching variables on leachate quality including:

-- moisturization water quality (Farris, 1979; Metcalf and Eddy, 1975; Fox, 1982a; Stanley et al., 1981; Jackson and Jackson, 1982)

-- particle size (Glaze, 1981; Silviera et al., 1978; Fransway, 1980)

-- solid-to-liquid ratio (Silviera et al., 1978; Saether, 1980; Glaze, 1981; Fransway, 1980)

-- compaction and bulk density (Holtz, 1976; Farris, 1979; Malek, 1981)

-- equilibration time (Silviera et al., 1978; Stollenwerk, 1980; Glaze, 1981)

-- wet-dry cycles (Stollenwerk, 1980)

-- microbial interactions (Brierley and Brierley, 1981; Klein et al., 1981; Rogers et al., 1981)

Other studies have investigated the extra-pile transport of leachates. Glaze (1981) and Runnells and Esmaili (1981, 1982) have studied the effect of local geologic materials on leachate composition and transport. Leenheer and Stuber (1981) and Leenheer et al. (1981) have studied chemical and physical interactions between an in situ retort water and a soil, and Routson and Li (1980) investigated the sorption of collidine on a soil.

These laboratory studies of extra-pile transport have been complemented by field studies at actual retorting sites. Battelle Pacific Northwest Laboratories has conducted field reconaissance studies at Anvil Points to determine the effect of oil shale operations on water quality. The Anvil Points field work has been completed, and some preliminary results from that site have been published or are in preparation (Wildung et al., 1980-81; Riley et al., 1981; Garland et al., 1981).

Still other investigators have attempted to develop water and solute transport models that simulate percolation and runoff. Ward et al. (1971) used a water and salt balance approach to predict TDS concentrations in runoff. Ward and Reinecke (1972) and Margheim (1975) developed a quasi-empirical model for TOSCO spent shale that estimates the quality of surface runoff resulting from snowmelt.

Percolation also has been modeled by several investigators. Margheim (1975) developed a chemical model that predicts the concentration of TDS and Mg, SO_4, Na, and Ca in percolation through TOSCO II spent shale. Fransway (1980) used an existing chemical model to predict EC, Ca, Mg, K, Cl, HCO_3, and CO_3 in percolates from Paraho direct-mode spent shale. Bloomsburg and Wells (1978) developed a finite-element model that describes the movement of moisture through a Paraho spent shale disposal pile, and they verified it using seepage ponds at Anvil Points. Ramirez (1981) is developing a mass-transfer model that will describe solute transport in a spent shale pile and Battelle Pacific Northwest Laboratories is developing a geochemical model of leachate quality (Wildung et al., 1977-1981).

Research also has been conducted on the biological effects of surface spent shale leachates. Paraho, TOSCO II, and Union B leachates have tested negative in the Ames/Salmonella mutagenicity assay (Dickson and Adams, 1980). Cleave et al. (1979, 1980) found that Paraho and Union B leachates stimulated the growth of their test alga, Scenedesmus, and that Paraho leachates were more biostimulatory than Union B leachates. Bergman (1980) found that Paraho spent shale leachates were not toxic to juvenile fathead minnows and adult Daphnia pulicaria in a short-term static bioassays.

In Situ Spent Shale Leachates

This issue has been investigated in a number of modeling studies (Mehran et al., 1980; Robson and Saulnier, 1981; Brown et al., 1977) and laboratory studies (Stollenwerk, 1980; U.S. DOE, 1980; Jackson et al., 1975; Peterson et al., 1981, 1982; Amy, 1978; Amy and Thomas, 1977; Amy et al., 1980; Hall, 1982; Fox, 1982a; Bethea et al., 1981; Kuo et al., 1979; Parker et al., 1980; Krause et al., 1980; Leenheer and Stuber, 1977).

Early studies (Jackson et al., 1975; Amy, 1978; Parker et al., 1977) and analyses based on them (Fox, 1979; Fox, 1980b) suggested that high concentrations of total dissolved solids (TDS) and certain trace elements would be leached from in situ spent shales and transported in local aquifers, posing a health and economic problem to local water users in the Upper Colorado River Basin. These early conclusions were based on leaching studies conducted on simulated spent shales (Amy, 1978; Jackson et al., 1975; Parker et al., 1977) that are now known to be chemically different from field samples (Smith et al., 1978; Burnham et al., 1980; Park et al., 1979; Peterson et al., 1982) and on unrealistic laboratory simulations of field conditions in which distilled water and very small particle sizes were used.

Recent studies at Los Alamos National Laboratory (LANL) (Peterson et al., 1981, 1982) demonstrate that the impact of in situ leaching on groundwater quality may be less significant than previously believed. These studies confirm earlier work by Park et al. (1979) and Kuo et al. (1979) that high temperatures and long residence times at elevated temperatures common in in situ retorts, 800 to 1000 C and days to years, decrease the solubility of most elements studied by about an order of magnitude. Among the important trace elements, only V showed increased solubility at elevated temperatures. These studies also indicate that secondary solubility controls may actually improve groundwater quality by providing anions such as sulfate or carbonate which precipitate many toxic metals. The LANL work suggests that of the elements studied, only V, Se, and Pb may pose an environmental hazard.

Characterization, field migration, and mechanistic studies have been conducted on in situ spent shale leachates. The characterization studies have focused on elemental analyses of leachates from Occidental (Peterson et al., 1982; Kuo et al., 1979; U.S. DOE, 1980) and Geokinetics (Krause et al., 1980) retorts. No data are available on organic or organometallic species in field leachates. However, two studies have reported organic analyses for simulated in situ samples from the Lawrence Livermore National Laboratory (LLNL) and Laramie Energy Technology Center (LETC) retorts (Hall, 1982, 1982; Amy, 1978). These studies reveal that in situ leachates have a pH of 7 to 11 and that organic nitrogen, phenols, V, Pb, and Se may occur at environmentally significant concentrations.

The field studies (Jackson et al., 1975; Stover, 1981; Sharrer, 1981; Virgona et al., 1979) have monitored the effect of actual field in situ experiments on local groundwater quality. In these studies, the retorting site is surrounded by a series of monitoring wells which are periodically sampled over long periods of time. Much of this work is too new to yield any significant conclusions.

The work by Jackson et al. (1975) and Virgona et al. (1979) was conducted at LETC's true in situ experimental site at Rock Springs, Wyoming. Much of this work was inconclusive due to analytical problems, inadequate information on local geohydrology, and the absence of an analytical framework to evaluate the data. There were no consistent changes in quality, except that carbonate, bicarbonate, TOC, and B increased in most wells. Boron concentrations remained high following retorting.

Industry self monitoring programs are in progress at Occidental's Logan Wash site (Stover, 1981) and at Geokinetics' Seep Ridge site (Sharrer, 1981). Meglen and Erickson (1981) have used pattern recognition techniques to analyze water quality data from the Occidental site. They found that few water quality changes could be attributed to the transport of leachates from the retorts, and the only statistically significant changes that they reported were increased

Li concentrations at one stream site, increased B, K, and alkalinity at two satellite wells close to the retorts, and increased Mg, SO_4, and K at one distant satellite well.

The mechanistic studies have investigated the effect of various retorting and leaching variables on leachate composition. Several studies have considered the effect on leachate quality of retorting conditions, including temperature, time at temperature, and inlet gas composition (Park et al., 1979; Bethea et al., 1981; Peterson et al., 1982). These studies employ small laboratory reactors in which conditions can be carefully controlled. Other investigators (Amy, 1978; Amy and Thomas, 1977; Amy et al., 1980) have used samples from larger, simulated in situ retorts to study the effect of retorting on leachate quality.

Other mechanistic studies have focused on thermodynamic and kinetic leaching variables. A wide range of variables and conditions has been studied, including: (1) leach water temperature (Amy, 1978; Bethea et al., 1981); (2) water quality (Amy, 1978; Bethea et al., 1981; Peterson et al., 1982); (3) particle size (Amy, 1978; Jackson et al., 1975); (4) leaching atmosphere (U.S. DOE, 1980); (5) wet-dry cycles (Peterson et al., 1982); (6) shale-water contact time (Amy, 1978; Peterson et al., 1982); (7) groundwater flow velocity (Hall, 1982); (8) pore volume (Hall, 1982; U.S. DOE, 1980; Stollenwerk, 1980); (9) and solid-to-liquid ratio (Amy, 1978).

Several investigators have developed water and solute transport models of in situ retorts and/or surrounding aquifers. Water movement through an abandoned in situ retort has been modeled by Brown et al. (1977); by Mehran et al. (1980); and by Robson and Saulnier (1981). These studies reveal that saturated-unsaturated flow and fracture systems should be simulated in future work. All of these studies were limited by the availability of adequate laboratory and field data. Others have or are developing solute transport models of the retort and aquifer systems. Hall (1982) and Amy (1978) have developed mass-transfer models for spent shale TOC, and new work at Denver Research Institute will attempt to simulate other chemical species (Fitzpatrick, 1982).

Chapter 2

RETORTING TECHNOLOGY

The leaching characteristics of spent shale depend on the mineralogy and chemical composition of the raw shale and on the specific retorting process. Retorting parameters such as temperature, atmosphere, time at temperature, and particle size determine spent shale mineralogy and, hence, its leaching characteristics.

The purpose of this section is to briefly describe the various surface and in situ retorting processes that are being considered for commercialization. These processes are listed and described in Table 2-1 together with spent shale characteristics. The parameters summarized on this table are important in defining the leaching characteristics of the spent shale and will be referred to in subsequent discussions. Leaching studies have been conducted on raw and spent shales from most of these processes, and they will be discussed in Chapters 3-5.

The surface processes reviewed here span a range of operating conditions. Maximum temperatures range from about 480 C to over 750 C and residence times at temperature range from a few seconds to several hours. The in situ processes generally operate at higher temperatures than surface processes because the retorts are nearly adiabatic, and maximum temperatures within the retorts cover a much wider range. Residence times at temperature in these in situ processes are much longer than in surface processes and range from many hours to several days. These variables, together with retorting atmosphere, are important in determining the mineralogy and, hence, the leaching characteristics of the resulting spent shale. The reader should realize that these processes are under development; changes may be expected in process design, in optimum operating parameters, and hence, in product characteristics, as the industry develops.

This summary is not intended to be an exhaustive review of retorting technology. Others have recently prepared such reviews (Ranney, 1979; Baughman, 1978; Jee et al., 1977; Shih et al., 1979; Fox 1980b; Considine, 1977; Nowacki, 1981; EDC, 1981), and the reader is referred to these reviews or to the literature references noted on Table 2-1 if more information is required. Rather, the purpose of this overview is to provide a framework for interpreting leaching data.

SURFACE PROCESSES

Surface retorts are aboveground kilns in which crushed oil shale is thermally decomposed (pyrolyzed). The vessel in which the pyrolysis reaction occurs is called a "retort". There are two broad classes of surface retorting processes -- direct and indirect. The indirect processes are those in which heat generation and oil production occur in separate vessels. Typically,

TABLE 2-1

Retorting and Spent Shale Characteristics for Some Near-Commercial Surface and In Situ Processes.

	Retorting Characteristics				Spent Shale Characteristics				
						Particle Size (%)			
Process	Raw Shale Feed Size (cm)	Temperature (°C)	Atmosphere	Heat Source	Residual Organic Carbon (%)	% Gravel (+4.8 mm)	% Sand (0.074-4.8 mm)	% Silt and Clay (0.074 mm)	Reference
Surface (Direct)									
Paraho	+0.6 to -7.6	Pyrolysis 500 Combustion 750	Diluted recycle gas	Internal combustion of char and recycle gas	2.3	55	23	22	Nowacki, 1981; Fruchter et al., 1980; Heistand et al., 1980
Surface (Indirect)									
Superior	+0.6 to -7.6	Pyrolysis 480-540 Combustion (b)	Recycle gas	External combustion of char and externally and indirectly heated recycle gas	low	-	-	-	Jee et al., 1977; EDC, 1980; Knight and Fishback, 1979
Union B	+0.3 to -5.1	Pyrolysis 510-540	Recycle gas	Externally heated recycle gas	4.3	74	16	10	Nowacki, 1981; Cloninger, 1978; Snyder and Pownall, 1978
TOSCO II	-1.3	Pyrolysis 480	Autogenous	Externally heated ceramic balls	5.4	5	57	38	Nowacki, 1981; Vawter, 1978
Lurgi	-0.6	Pyrolysis 510 Combustion 650	Recycle gas	External combustion of char on spent shale	0.5[f]	0	20	80	Rio Blanco, 1981a
Chevron STB	-0.6	Pyrolysis 500 Combustion (b)	Recycle gas	External combustion of char on spent shale	low	-	-	-	Chevron, 1981; USDI, 1983
In Situ (Modified)									
Occidental	+0.5 to -60[d]	Pyrolysis 500 Combustion 500-<1200[a]	Air/Steam	Internal combustion of char on spent shale	0.1[c,e]	85[d]	15[d]	0	Campbell et al., 1981; McCarthy, 1976; Harak et al., 1974; Hall, 1982
In Situ (True)									
Geokinetics	(b)	Pyrolysis 500 Combustion 500-<1200[a]	Air	Internal combustion of char on spent shale	low[e]	-	-	-	Lekas, 1979 1981

[a] Wide ranges have been observed (Campbell et al., 1981) in field temperatures. The work of Smith et al. (1978) and Park et al. (1979) indicates that temperatures will be less than the fusion temperature (1200 C).

[b] Unknown.

[c] Based on 11 runs of the Lawrence Livermore National Laboratory simulated in situ retorts (Campbell, 1981).

[d] Based on data from the Laramie Energy Technology Center 10-ton (Hall, 1982) and 150-ton retort (Harak et al., 1974).

[e] Field values may be higher due to incomplete combustion.

[f] Bates, 1981.

heat is transferred to the crushed shale in the pyrolysis vessel by an externally or "indirectly" heated gas or solid. In these processes, the atmosphere within the retort is reducing. Carbon or char formed on the spent shale during pyrolysis may be combusted to generate heat outside of the retort (Lurgi, Chevron), or it may remain on the spent shale (Union B, TOSCO II). In the latter case, heat is generated by combustion of gases. Indirect-heated processes include the Fischer Assay, TOSCO II, Lurgi, Union B, Paraho indirect, Chevron STB, Shell Spher, Superior indirect, Galoter, and Petrosix retorts. The direct processes are those in which heat is supplied by the combustion of char and recycle gases within the retort and following pyrolysis. Thus, both reducing and oxidizing atmospheres may exist within direct-heated retorts. Examples of direct-heated processes include the Paraho direct, Union A, Union SGR, and Superior direct retorts.

Paraho-Direct

The Paraho retort consists of a vertical kiln that may be operated in either the direct or indirect mode (Figure 2-1) as described by Jones (1976). The studies reviewed here used products from the 200 bbl/day Paraho direct-mode 23-m high semiworks retort operated by Development Engineering, Inc. at Anvil Points, CO. The retort operates as a countercurrent, plug-flow reactor; recycle gas moves upward through the retort while the solids move downward. Shale entering the top of the retort is initially heated by rising hot gases. It next passes into the pyrolysis zone where the organics are thermally distilled. The pyrolysis heat is produced in the combustion zone from burning of char and recycle gas. The distilled vapors are swept upward, out of the retort, and the oil is separated from the gas by a coalescer and electrostatic precipitator. The oil and water are separated by settling. The hot spent shale passes through the cooling zone and is discharged at the bottom of the retort. In this retort, the maximum temperature is 750 C, and both oxidizing and reducing conditions occur.

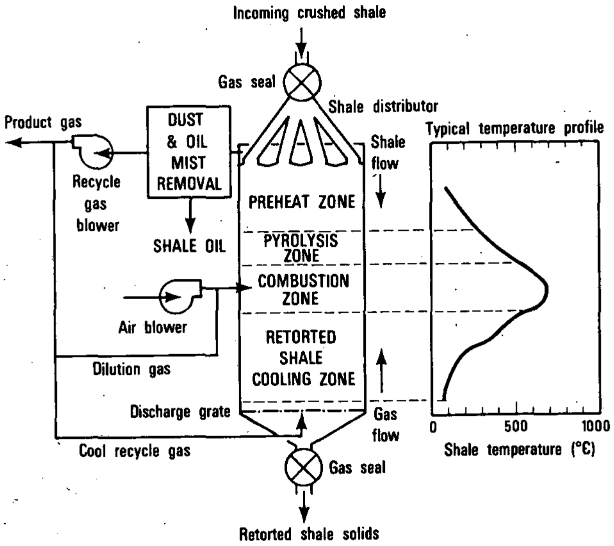


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Figure 2-1. Schematic of Paraho direct-mode retort (Fox et al., 1982).

Superior Indirect

The Superior retort (Figure 2-2) has been proposed as an integral part of a multi-mineral recovery process in which nahcolite, alumina, soda ash, and shale oil are byproducts. Nahcolite is recovered from the raw shale prior to retorting, and alumina and soda ash are recovered from the spent shale following retorting (Weichman, 1976).

The Superior retort is a circular, travelling-grate retort similar to those used for the sintering of iron oxide, and it may be operated in either the indirect or direct mode (Knight and Fishback, 1979). The indirect process was proposed in the Superior land exchange (USDI, 1979) and, therefore, is discussed here. In the indirect mode, recycle gas is externally heated in an "indirect heater" and introduced into the pyrolysis zone at temperature while in the direct process, pre-heated combustion air and hot recycle gas are burned within the pyrolysis zone in "direct-heating burners."

The moving grate transports shale through various processing zones arranged in a circle. These zones are: (1) loading and unloading, (2) pyrolysis, (3) carbon recovery, and (4) shale cooling (Knight and Fishback, 1979). Crushed and sized raw shale is fed continuously onto the rotating circular grate through inert-gas-purged mechanical seals. This raw shale is rotated into the pyrolysis zone where it is heated to about 500 C with indirectly heated recycle gas. Pyrolysis vapors are swept out of this section, cooled by direct-contact spray, and the oil recovered in a separator-condensor system. Next, char on the spent shale is partially combusted by controlled oxidation using either preheated air or oxygen. The spent shale is then cooled with recycle gas and air. Recycle gas is heated in the cooling zone by recovering sensible heat from the hot spent shale. The shale is further cooled by ambient air which is preheated for use in the carbon recovery section. Spent shale is then discharged by a water seal which wets it for dust control.

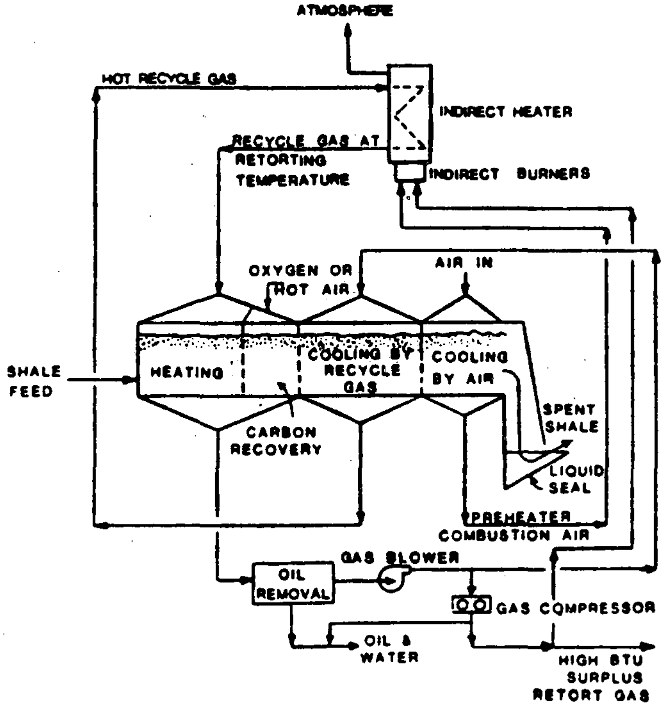

Figure 2-2. Schematic of the Superior circular grate retorting process, indirect-heated mode (Nowacki, 1981).

Union B

The Union Oil Company has developed three retorts -- Union A, Union B, and Union Steam Gas Recirculation (SGR). The Union B retort has been proposed for a 10,000 BPD field demonstration at the Union Long Ridge site (Union, 1979) and, therefore, is discussed here.

The Union B (Figure 2-3) retort is a vertical kiln. Shale is moved through it by a dual-piston rock pump, countercurrent to externally heated recycle gas. Raw shale is introduced at the bottom of the retort and hot recycle gas at the top. The shale is pyrolyzed by hot recycle gases as they move upward. The pyrolysis vapors are cooled as they pass downward over the incoming shale. Condensed oil and gases leave the retort through vertical slots in the lower retort wall. Maximum operating temperature occurs at the top of the retort. Spent shale overflows to a discharge chute and is removed through a water seal. The spent shale temperature is about 93 C, and its surface is dry as it enters the disposal area (Snyder and Pownall, 1978).

The SGR and A retorts are very similar to the B retort. The SGR uses the Union B design but includes a separate gasification vessel in which oxygen and steam are introduced to gasify the residual carbon. The A also uses the Union B design but is operated in the direct-mode, similar to the Paraho direct. Both the SGR and A retorts use the char combustion gases for pyrolysis instead of the recycle gas. The spent shales from these three processes will differ due to different retorting conditions.

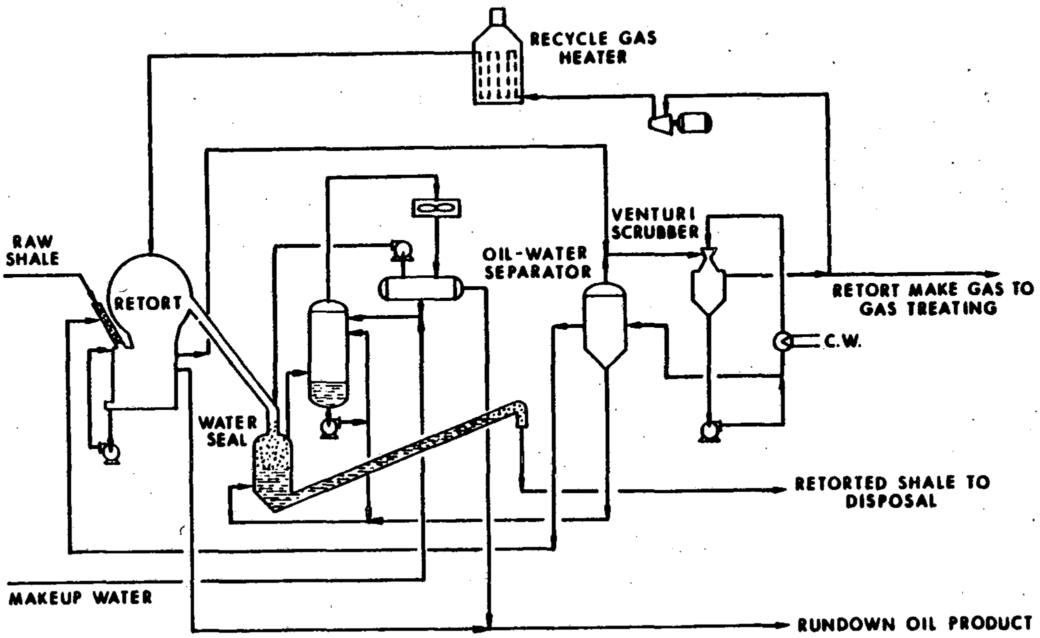

Figure 2-3. Schematic of the Union B retorting process (Nowacki, 1981).

TOSCO II

This retort (Figure 2-4) is an insulated ball mill in which pyrolysis is achieved by direct contact between hot ceramic balls and preheated oil shale. Raw shale is fed from a surge hopper into a series of pneumatic lift pipes where it is fluidized by a stream of hot flue gas from the ball heater. This raises the temperature of the shale to about 260 C. The preheated shale is then separated out in settling chambers and cyclones and is fed into a rotating pyrolysis-drum retort along with hot ceramic balls from the ball heater. This retort is an efficient mixing device, and heat is transferred from the balls to the shale, raising the shale to pyrolysis temperatures. This contact between balls and shale also crushes the shale to a fine powder. The pyrolysis vapors, spent shale, and ceramic balls leave the retort together and are separated in a perforated rotating trommel. Shale powder passes through the perforations in the trommel. The balls are purged of dust, lifted into a bucket elevator, and returned to the ball heater (a direct-contact heat exchanger). The pyrolysis vapors pass through an accumulator and a fractionator where light oil, naphtha, and heavy oil are recovered. Hot flue gases from the fractionator are cycled to the ball heater. Spent shale leaves the retort at around 480 C and goes through a special heat exchanger designed to cool the spent shale and to generate steam for plant use. The spent shale is then cooled further by direct contact with water and moisturized to about 14% by weight (Jee et al., 1977; Nowacki, 1981).

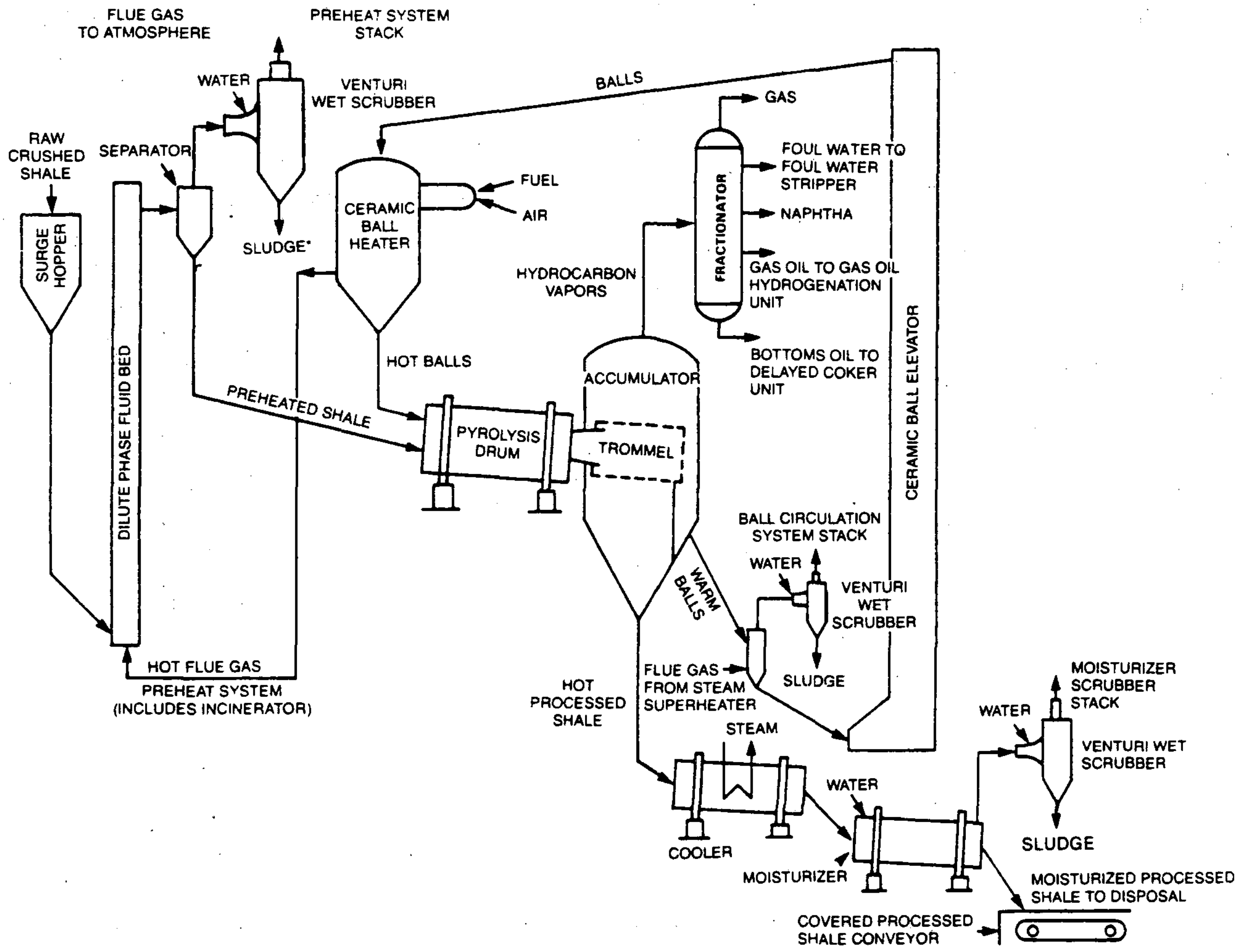

Figure 2-4. Schematic of TOSCO II retorting process (OTA, 1980).

Lurgi

This retort (Figure 2-5) is a screw mixer in which pyrolysis is achieved by direct contact between hot spent shale and raw shale. Crushed raw shale from the feed bin is fed to the screw mixer where it is mixed with six to eight times as much hot spent shale (Nowacki, 1981). This raises the raw shale to about 480 to 540 C. Pyrolysis vapors from the mixer pass through several cyclones where entrained dust is removed and condensation/scrubber towers where heavy oil, middle oil, light oil, and retort water are recovered.

The mixture of solids from the screw mixer falls by gravity into the surge bin and then into the bottom of the Lurgi lift pipe where hot air at about 450 C and auxiliary fuel are added. The gas lifts the spent shale from the bottom of the pipe to the top and residual carbon is burned, raising the temperature of the combined gas-solids mixture to about 650 C. A portion of this hot spent shale falls into the collecting bin and then into the mixer, thus completing the cycle. The remainder enters the air preheater where lift-pipe combustion air is preheated and then into a steam generator. The remaining gas and spent shale pass through a cyclone and an electrostatic precipitator before being vented. Spent shale removed in the various cyclones and the precipitator go to the spent shale cooler where the spent shale is cooled to about 90 C and then to the moisturizer for final wetting prior to disposal (Rio Blanco, 1981).

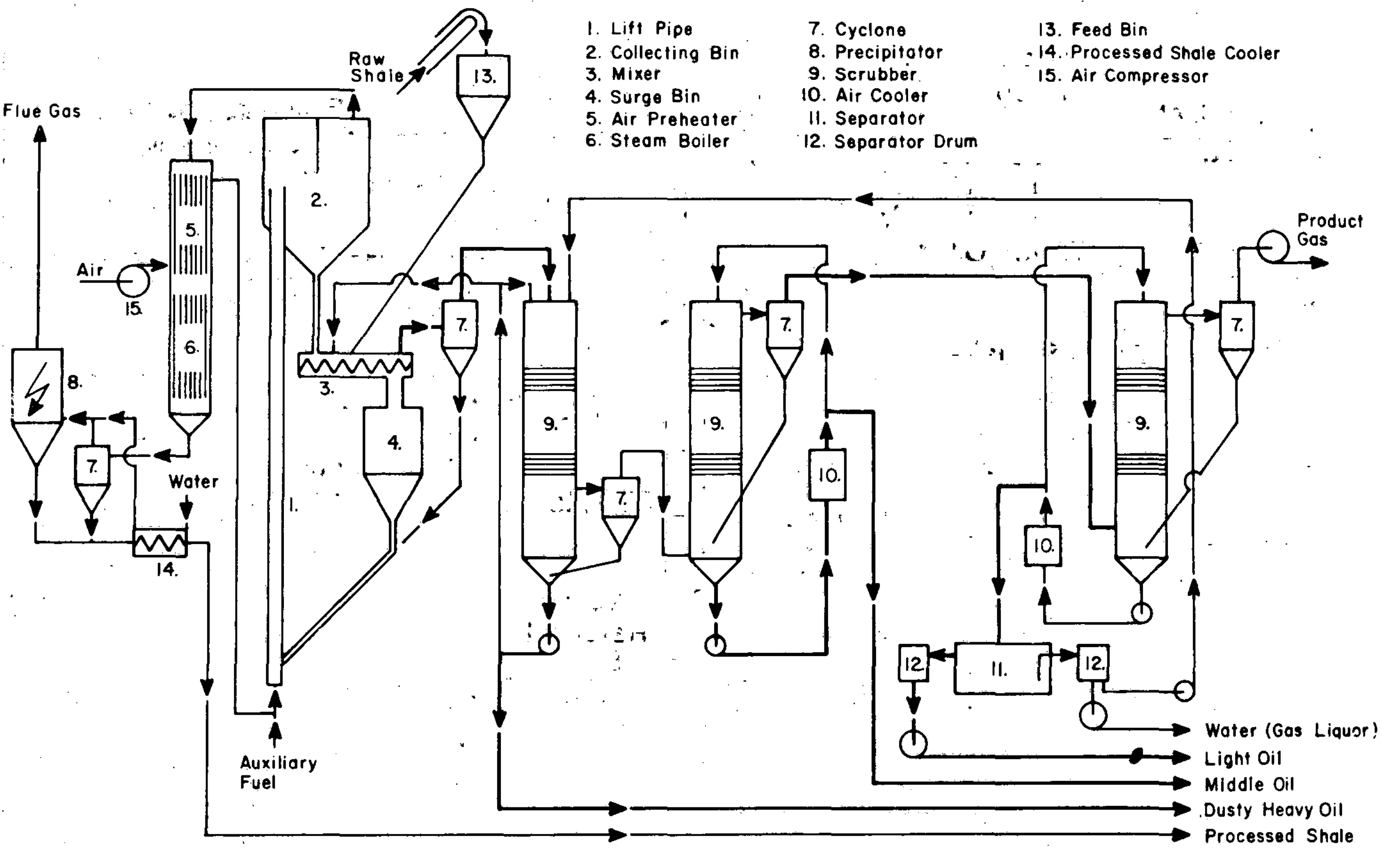

Figure 2-5. Schematic of Lurgi retorting process (Rio Blanco, 1981a).

Occidental Modified In Situ Process

The in situ recovery of shale oil by the Occidental MIS process involves the underground pyrolysis of large chambers of rubblized shale. These chambers are constructed by mining out about 20% of the volume of the retort and blasting the balance so that the entire chamber is filled with fractured rock. A commercial-sized retort will measure about 100 m by 50 m in plan and 120 m high. Oil is recovered from such a retort, shown in Figure 2-7, by initiating combustion at the top of the retort with an external fuel supply and propagating the reaction zone, which consists of a pyrolysis zone and a trailing combustion zone, down the packed bed of shale with input gas. The volatile hydrocarbons condense in the cool region at the bottom of the retort and are pumped to the surface.

Occidental has tested six experimental retorts at Logan Wash, Colorado. Leaching studies have been conducted on materials from Retort 3 which is briefly described here. Retort 3 was operated between February and July of 1975 in air-recycle gas mode. Yield was around 60% Fischer Assay. This retort was cored in December 1978, and the spent shales have been characterized and subjected to leaching studies (U.S. DOE, 1980; Peterson et al., 1981, 1982; Kuo et al., 1979; Stollenwerk, 1980).

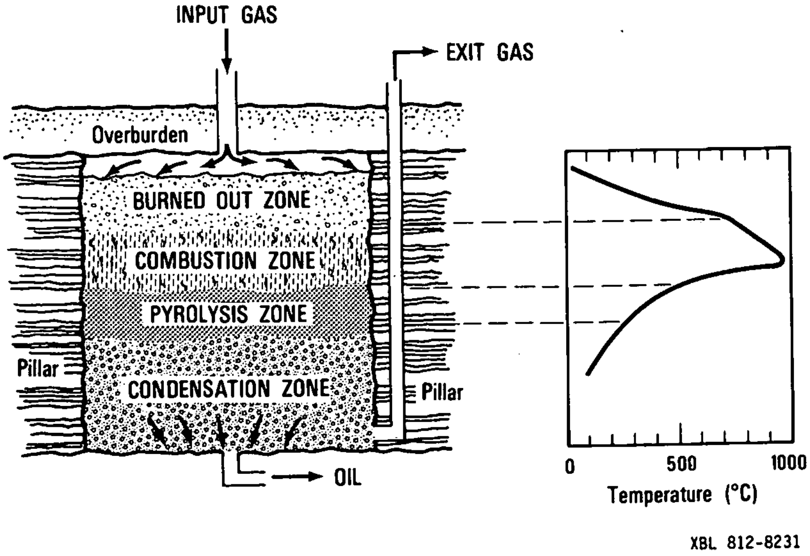

Figure 2-7. Schematic of the Occidental modified in situ retorting process (Fox et al., 1982).

Geokinetics Horizontal In Situ Process

The Geokinetics process, shown in Figure 2-8, is designed for areas where oil shale beds are relatively thin and close to the surface. Permeability is created by explosive fracturing which uplifts the surface by about 3 m. A commercial-sized retort may measure about 70 m long by 70 m wide by 10 m thick. Oil is recovered from these retorts by igniting the shale bed near the air injection well and driving the reaction zone horizontally through the fractured bed with input gas. The volatile hydrocarbons condense ahead of the reaction zone and collect in the recovery wells where they are pumped to the surface.

Geokinetics has burned 19 experimental retorts to date (Lekas, 1981). Raw and spent shale cores were taken from Retort 16, and leaching studies are in progress (Bates, 1981). Other samples were collected from Retorts 1 and 11 and subjected to mineralogical and leaching studies (Leenheer and Stuber, 1977; Krause et al., 1980).

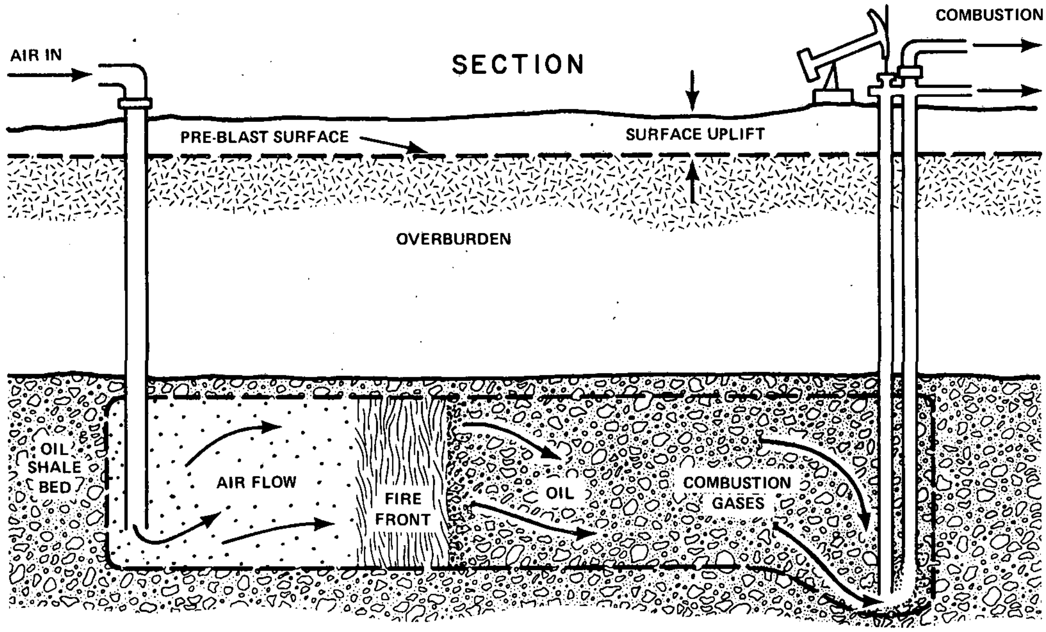

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Figure 2-8. Schematic of the Geokinetics retorting process (Fox et al., 1982).

Chapter 3

RAW SHALE

Large quantities of raw oil shale will be permanently or temporarily stored or disposed of on the surface where it may be leached by rainfall and snowmelt. The resulting leachates may readily percolate to groundwater due to the high permeability of these piles, or they may runoff of the piles and enter surface streams. Water sprays used to control dust also may produce leachates or effect the quality of precipitation leachates. And mine waters associated with freshly mined shale may drain and reach water courses.

In spite of the large quantities of raw shale that must be handled, stored, or disposed of during oil shale production, raw shale leachates have received relatively little attention due to the more controversial spent shale issue and to a belief by many that raw shale leachates are benign. Industry's position has long been that raw shale leachates will be similar to natural runoff because the soil, talus slopes, and outcrops in oil shale regions are weathered oil shale. However, recent research results suggest that freshly mined and/or crushed oil shale may release environmentally significant quantities of some elements for long periods of time. However, the potential significance of these observations at any specific development site have not been assessed.

The next section will identify and discuss the quantities and methods of raw shale disposal at some proposed retorting sites. Subsequent sections will review and assess research completed on raw shale composition and leaching. Chapter 7 will use this information as a basis for identifying future research needs and priorities.

RAW SHALE DISPOSAL PROCEDURES

Large quantities of raw shale will be permanently or temporarily stored aboveground during in situ or surface retorting operations. Some industry proposals summarized from development plans and environmental permits are presented in Table 3-1. A review of this information indicates that large quantities of raw shale (32,000,000 tons) covering as much as 325 acres in 10 years for a 76,000 BPD MIS/TOSCO plant, will be stored at the surface. This raw shale originates from mine development and site construction, from dust control devices, from surge capacity storage for retort operations, and from retort feed preparation. The material will be stored or disposed of in side-hill or cross-valley fills or in conical surge piles at the plant site. Fines from dust collection and retort feed rejection will be co-disposed with the spent shale. Runoff from these storage areas will be collected in ditches and possibly discharged to natural drainages.

TABLE 3-1

A Summary of Some Proposed Raw Shale Disposal Plans.

Process/Location	Commercial Production[a]	Raw Shale Storage and Use During Development and Construction Phases	Raw Shale Storage During Commercial Operation
Tract C-b TOSCO II with room-and-pillar mining (C-b Shale Oil Project, 1976)	66,000 TPD raw shale 45,000 BPD oil	• During the 3-yr development mining period, 5,000-6,000 TPD of 6-12 in. raw shale will be stockpiled in Cottonwood Gulch on 35-40 acres. A catchment dam will be located below the stockpile. During plant construction, the pile may contain in excess of 10,000,000 T and occupy an area of 80 acres. Piles will be benched, watered, revegetated, or covered until used.	• Coarse-ore stockpile will have a live operating capacity of 500,000 T and a total capacity of 2,000,000 T and will occupy 35 acres in Cottonwood Gulch. A water mist will be used to control dust.
Tract C-b Modified in situ without aboveground retorting (C-b Shale Oil Venture, 1977)	57,000 BPD oil	• Direct disposal of raw shale in nearby gulches with no surface retorting. About 25,000,000 T of mined shale (16,000,000 T from shaft sinking) will be crushed and compacted for construction fill in Cottonwood Gulch.	• The remainder of Cottonwood Gulch will be filled with 40,000,000 T shale. After 3.4 yrs, disposal operations, at a rate of 14,000,000 T/yr, will be shifted to Sorghum Gulch. Underground disposal of the raw shale also will be considered.
Tract C-a TOSCO II and gas combustion retorting with open-pit mining (Rio Blanco, 1976)	119,000 TPD raw shale 55,800 BPD oil	• During Phase I, primary crushed shale will be stockpiled in a conically shaped pile containing 100,000 T of -6 in. crushed shale. Just prior to commercial operation, the pile will contain 300,000 T. During Phase I, one day's retort feed (10,700 TPD) of -3/8 in. crushed shale and up to 63,000 additional tons will be stockpiled in an outdoor "reserve storage pile." Overburden and subore will be segregated and compacted to 31,000,000 yd^3 in an outdoor storage pile.	• Primary crushed ore stockpile will be an open storage facility consisting of two windrow piles, 65 ft high, 180 ft wide, and 1,300 ft long (5 acres) and containing 300,00 T. One day's feed may be stored in an outdoor reserve storage pile. Overburden and subore will undergo primary crushing prior to disposal.
Tract C-a Lurgi with open-pit mining (Rio Blanco, 1981)	4,400 TPD raw shale 2,230 BPD oil	• Crushed oil shale and crushed overburden for retort startup are stored in an enclosed building. During Phase I, 5.2 x 10^6 bcy overburden (50% in subore) and during Phase II, 4.2 x 10^6 bcy overburden (30% subore) will be generated. Some of this will be used for construction, and the rest will be disposed of.	• None proposed.
Tract C-a modified in situ with TOSCO II (Rio Blanco, 1977)	40,000 TPD raw shale 76,000 BPD oil	• During the first 8 yrs, 5,000,000 T of run-of-mine shale (-24 in) will be stored in 65 acres in the "ore disposal pile." During the following 2 yrs, 27,000,000 T shale crushed to -8 in. will be stored in 260 acres. Runoff from these piles will be collected in ditches and discharged to natural drainages.	• Primary crushed ore will be stored in a pile that contains 100,000 T of -8 in crushed shale. A 24-hr supply of retort feed (-3/8 in.) is stored in an open "reserve storage pile" (14,000 T).
Colony/Dow West TOSCO II with room-and-pillar mining (USDI, 1975)	61,000 TPD raw shale 47,000 BPD oil	• Coarse ore stockpile may contain up to 5,000,000 T of oil shale and cover 25 acres.	• Coarse-ore stockpile will contain about 1,500,000 T oil shale to a height of 200 feet and cover 15 acres. Raw shale dust and fines will be disposed of with the spent shale.

TABLE 3-1. Continued.

Piceance Creek Basin Superior with room-and-pillar mining (USDI, 1979)	11,600 BPD oil	• About 13,000 TPD raw shale from the secondary crushers (-3 in.) will be stored. The shale storage area, at the end of 3 yrs, will contain about 14,000,000 T covering 80 acres to a depth of 80 feet. This shale will include nahcolite stripped shale, fines, and other raw shale.	• The shale pile will be reduced to 5,500,000 T over 5 yrs by startup of the pyrolysis unit and slowly depleted over the next 18 yrs.
Tracts U-a/U-b Superior, Union B, and TOSCO II with room-and-pillar mining (White River Shale Project, 1981)	176,740 TPD raw shale 106,300 BPD oil	• Secondary crushed raw shale (-4 in.) will be stored in a single, conical pile with a capacity of 500,000 T and fines (-1/4 in.), about 2,700 TPD, will be stockpiled during Phase I (∿3 yrs). During Phase II (following 2.5 yrs), a second, 500,000 T secondary ore pile will be added, and the stored fines will be used in a TOSCO II retort. Excess mine development material will be disposed of in Southam Canyon along with spent shale.	• A third secondary ore pile of 500,000 T will be brought on stream for a total of 3. Shale fines will be stored for use in TOSCO II retorts.
Long Ridge Union B with room-and-pillar mining (Union, 1979a)	10,000 TPD raw shale 8,870 BPD oil	• Rock material from the Uinta and Green River Formation will be disposed of during access road construction in the spent shale disposal site. Mine development raw shale from enlarging the bench from 2 to 5 acres, from drilling the 10-ft ventilation shaft, etc. will also be disposed on the surface for ≤2.5 yrs. Some of this material will be covered with spent shale. Raw reject material (-1/8 in.) will be disposed of with spent shale (10% reject, 90% spent shale).	• Raw shale storage will be underground, in the mine. Raw shale fines, -1/8 in. retort feed reject, and dust will be disposed with the spent shale.

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[a] This column reports the quantity of raw shale, in tons per day (TPD), that will be mined and surface retorted and the quantity of oil, in barrels per day (BPD), that will be produced by the entire project (surface plus in situ). In situ projects with no aboveground retorting show no raw shale quantities because raw shale is not mined in these projects (i.e., Tract C-b in situ and Superior).

The quantities of raw shale and disposal procedures depend largely on mining and retorting methods. The type of material includes run-of-mine and other very coarse material from mine development and on-site construction, fines from dust control and retort feed preparation and primary and secondary crushed shale held in surge storage.

Mine Development

Raw shale produced during mine development (excavation of mine portal, shaft, adits, drifts; overburden removal; and site construction) may be either permanently or temporarily stored on site until retorting commences. Some of the material may be crushed and used for construction fill. The greatest quantity of raw shale will be exposed during open pit mining, such as that proposed for tract C-a (Rio Blanco 1976, 1981). Large amounts of overburden which includes low-grade oil shale from the Uinta and Green River Formation, must be stripped and stored at the surface until backfilling operations can safely begin (for 20 to 30 years). Other mining methods, such as room and pillar and sublevel caving, involve the shorter term storage, from 2 to 5 years, of lesser quantities of raw shale. In these other mining methods, mine development material from the excavation of shafts, adits, and drifts and on-site construction activities is temporarily stockpiled. Some of this material is then used when the retorts come on line.

Feed Preparation

Raw shale also originates from retort feed preparation and the need to provide surge capacity. Each retorting method requires a unique-sized feed material. This is provided by successively reducing the size of run-of-mine raw shale in primary, secondary, and/or tertiary crushers and screening the final material to remove fines (rejects). Fines from the Union B (Union, 1979a) and Paraho feedstocks (Stollenwerk, 1980) are generally less than 0.25 inches, and Union has estimated that about 10% of the rock mined and crushed will be fines (Union, 1979a). This fine material must be permanently stored on site or temporarily stored and reclaimed for use in a fines retort. In the White River Shale Project (1981) experimental plant, the fines reject from the first 3 years of operation of the Union B retort (2,700 TPD) will be reclaimed for subsequent processing in a TOSCO II retort. Thereafter, a more limited surge capacity will be required for fines. The Long Ridge Experimental Plant, on the other hand, calls for codisposal of raw shale fines and spent shale (Union, 1979a).

Leachate Collection and Disposal

There is no explicit discussion in any of the proposed industry plans for special environmental controls for raw shale leachates generated from raw shale storage or disposal piles. Controls for other solid wastes may be adequate to collect runoff from some piles. However, runoff from others may be discharged to natural drainages (Rio Blanco, 1977). No provisions for percolation control are evident.

All development plans include provisions for stormwater drainage at the plant site and at disposal areas where raw shale will be located. Typically, for large disposal piles away from the plant area, runoff originating outside of the area is routed around the disposal site; runoff from within the disposal area is collected behind a catchment dam for evaporation and/or plant use. Runoff from surge capacity and fines storage, which are located within the processing area, will be collected in the plant drainage system, treated for oil and/or grit and sediment removal, and reused in the process. Runoff from raw shale disposal piles will be diluted by runoff from other, much larger plant areas.

None of these plans discuss the generation and control of percolation from raw shale storage piles which may be more voluminous and contaminated than the runoff. Most rainfall and snowmelt will percolate through raw shale piles, rather than runoff, because they have a relatively high porosity and permeability due to large particle sizes, raw shale is less likely to consolidate under load, and the piles are not compacted. This is in contrast to spent shale piles where surface runoff may be relatively more important due to the lower permeabilities and porosities and higher densities by compaction.

RAW SHALE COMPOSITION

The geology, mineralogy, and chemical composition of oil shales of the Green River Formation have been extensively studied in the last half century. The mineral and chemical composition of raw shale is important in determining its leaching behavior and in interpreting and understanding the effect of retorting processes on spent shale composition and leaching characteristics. Accordingly, the elemental and mineralogic composition of raw shale from the Green River Formation is overviewed here. This review is not intended to be a critical analysis nor an exhaustive review of the available literature. Rather, it is presented to provide background information necessary to understand raw shale leaching, mineralogical changes that occur during retorting, and their importance to spent shale leaching. If the reader desires more detailed information, he/she is referred to the original literature references.

Formation and Stratigraphy

The Green River Formation, which contains the oil shale of interest, is composed primarily of lacustrine beds deposited from two large ancient Eocene lakes (Robinson, 1976). One of these lakes was north of the Uinta Mountains in southwestern Wyoming and northwestern Colorado. The other was south of the Uinta Mountains in eastern Utah and western Colorado. These two ancient lakes are now preserved in seven basins. The principal deposits of economic interest are in the Piceance Creek Basin and the Uinta Basin.

The Piceance Creek Basin contains the largest fraction of the total Green River Formation oil shale resource (Smith, 1980a). The stratigraphy and mineralogy of this basin are summarized in Table 3-2, and a diagrammatic cross-section is presented in Figure 3-1.

TABLE 3-2

Stratigraphy and Mineralogy of the Green River Formation,
Piceance Creek Basin, Colorado (modified from NAS, 1979).

Geologic Unit	Unit Subdivisions		Lithologic Description	Major Minerals	Major Minerals	Trace Minerals
Valley Alluvium 0' - 140'	-		Sand, gravel, clay	Quartz Dolomite	Analcine Calcite Albite K-feldspar	Illite Pyrite Siderite Aragonite
Uinta Formation 0' - 1250'	-		Mainly sandstone and siltstone with minor amounts of low-grade oil shale and barren marlstone			
Green River Formation	Parachute Creek Member 500' - 1600'	Upper Part of Parachute Creek Member				
		Mahogany Zone	Moderate- to high-grade oil shale	Dolomite Quartz	Albite Calcite	K-feldspar Aragonite Siderite Illite Pyrite Analcine Dawsonite
		Leached Zone	Low- to high-grade oil shale	Dolomite Albite Quartz Illite	K-feldspar Calcite	Pyrite Siderite Analcine Dawsonite
		Saline Zone	Saline minerals and moderate- to high-grade oil shale	Nahcolite Dolomite Quartz	Halite Dawsonite Albite K-feldspar	Pyrite Calcite Siderite Illite
	Garden Gulch member 0' - 900'		Mainly clayey shale and low- to moderate-grade oil shale	Quartz Dolomite	Albite Illite	Pyrite Calcite K-feldspar Siderite Analcine
	Douglas Creek member 0' - 800'		Mainly sandstone with minor amounts of limestone			
	Anvil Points member 0' - 1670'		Shale, sandstone, marlstone			
Wasatch Formation						

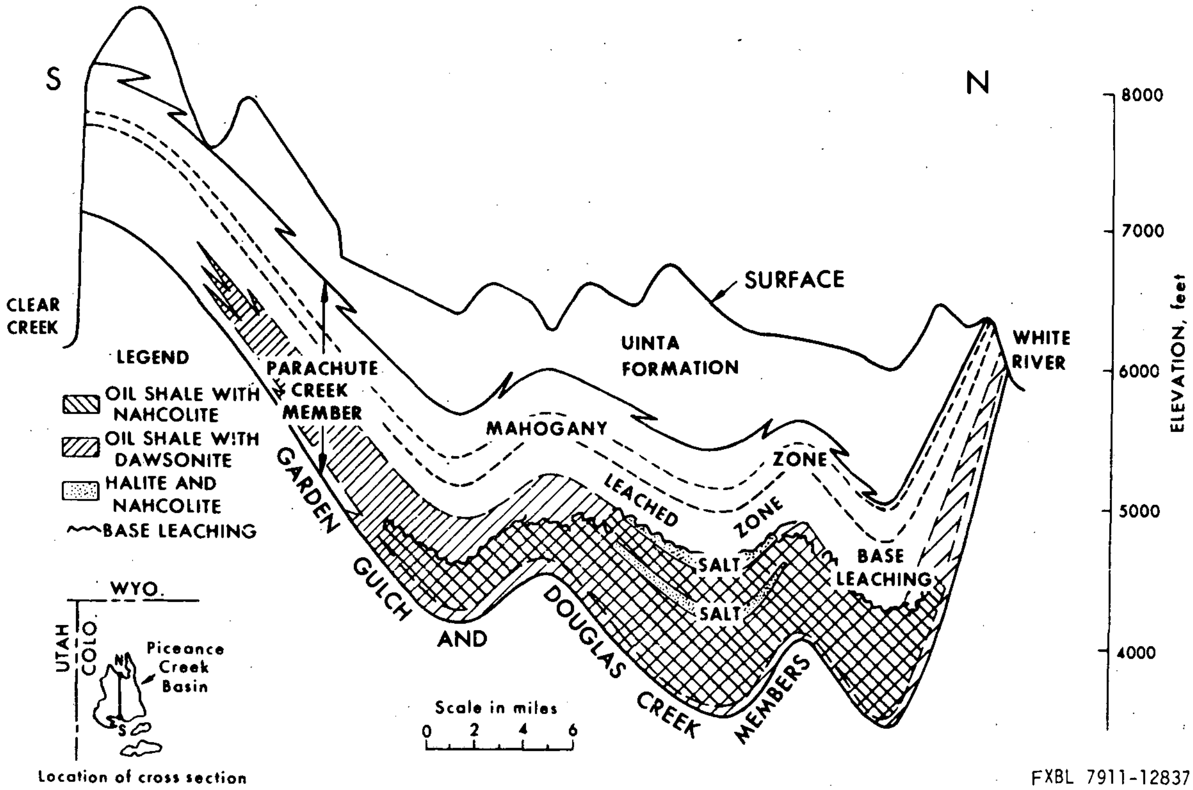

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Figure 3-1. South-north diagrammatic cross-section of the Green River Formation in Colorado's Piceance Creek Basin (Smith et al., 1978a).

This Basin consists of three major stratigraphic zones within the Parachute Creek Member (Coffin et al., 1971) as shown in Table 3-2. This Member is underlain by the overlapping Garden Gulch-Douglas Creek members which consist of clay-rich oil shale with low dolomite. The next zone, the saline zone, consists of relatively rich oil shale in a dolomite matrix with high concentrations of nahcolite and dawsonite. The next zone, immediately under the Mahogany Zone, is the leached zone which is similar in mineral content to the saline zone, except groundwater has removed the saline minerals over geologic time and left behind water-filled cavities (Hite and Dyni, 1967). The last zone in the Parachute Creek Member is the Mahogany Zone and overlying shales. The Mahogany Zone contains relatively rich oil shales and crops out around the Basin, providing easy access for mining (Smith, 1980a).

The stratigraphy and mineralogy of the Green River Formation in the Uinta Basin is similar to that in the Piceance Creek Basin. Stratigraphy of the Mahogany Zone and its overlying oil shales in Utah correlates precisely with the same stratigraphic section in Colorado (Trudell et al., 1970). However, oil shales below the Mahogany Zone in Utah tend to be lower grade than in Colorado and discontinuous (Smith, 1980a).

Mineralogy

The mineralogy of the Green River Formation is summarized in Table 3-2. Oil shale from the Green River Formation is a fine-grained sedimentary rock which contains appreciable quantities of organic material. The inorganic fraction is a marlstone which is composed principally of dolomite and calcite. It also contains significant quantities of quartz, Na- and K-feldspar, and illite. Some zones also contain elevated quantities of pyrite, nahcolite ($NaHCO_3$), and dawsonite ($NaAl(OH)_2CO_3$). The average mineral composition of Green River oil shale is summarized in Table 3-3.

TABLE 3-3

Chemical Composition of the Mineral and Inorganic Fraction of Green River Oil Shale

MINERAL COMPOSITION[a]

Mineral	Chemical Formula	Weight Percent of Total Minerals
Dolomite	$CaMg(CO_3)_2$	32
Calcite	$CaCO_3$	16
Quartz	SiO_2	15
Illite	(silica clay)	19
Na-feldspar	$NaAlSi_3O_8$	10
K-feldspar	$KAlSi_3O_8$	6
Pyrite	FeS	1
Analcime	$NaAlSi_2O_6 \cdot 2H_2O$	1
	TOTAL	100

ORGANIC COMPOSITION[b]

Element		Weight Percent of Total Minerals
Carbon		80.5
Hydrogen		10.3
Nitrogen		2.4
Sulfur		1.0
Oxygen		5.8
	TOTAL	100.0

[a] Smith, 1969

[b] Smith, 1961

The vertical variation of major mineral phases and Fischer Assay products in a core from the Naval Oil Shale Reserve near the depositional center of the Piceance Creek Basin is shown in Figure 3-2. This figure shows that the concentrations of dolomite and quartz are relatively constant throughout the corehole and typically account for 40 weight percent of the matrix. The other minerals, particularly calcite, are more variable.

Very little is known about the minor mineralogy of oil shale. The data which are available are summarized in Table 3-4. Desborough et al. (1976) hypothesized the mineral residence of several elements based on their occurrence in other crustal rocks and correlations among elements in several core samples. Giauque et al. (1980) investigated mineral residence by

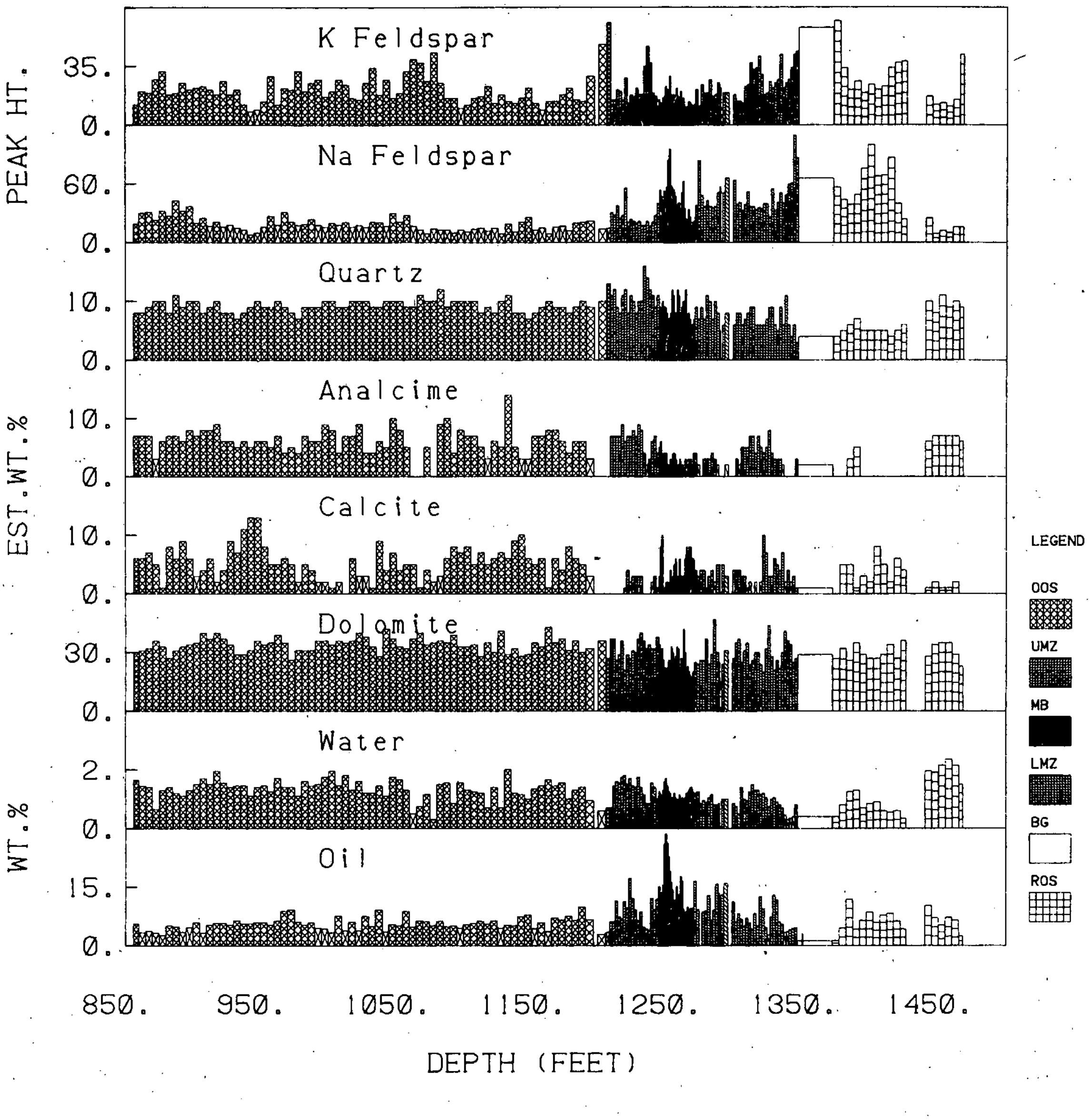

Figure 3-2. Vertical variation of K-feldspar, Na-feldspar, quartz, analcime, calcite, dolomite, Fischer Assay water yield, and Fischer Assay oil yield in core hole 15/16 from the Naval Oil Shale Reserve (Giauque et al., 1980). The legend is: OOS = overlying oil shale; UMZ = upper Mahogany Zone; MB = Mahogany Bed; LMZ = lower Mahogany Zone; BG = B-Grove; ROS = rich oil shale.

TABLE 3-4

Some Postulated Mineral Associations for Various
Major, Minor, and Trace Elements.

K-feldspar, Mg-siderite, Na-feldspar	Al, B, Ce, Co, Cr, Cu, Dy, Eu, Fe, Ga, Hf, La, Mn, Nd, Ni, Pb, Sb, Sc, Sm, Ta, Tb, Th, Ti, V, Y, Yb, Zn, Zr
K-feldspar, Mg-siderite	K, Rb
Na-feldspar, Analcime	Na
Calcite	Ba, Ca, Sr, inorganic C
Dolomite	Mg, Fe
Organic phase	As, H, Hg, Mo, N, Se, U, S
Unknown	Cd
Illite	F
Sulfides	Co, Cu, Ni, Pb, Sb, Zn, As, Mo, Se, Hg, S

Based on data presented by Desborough et al., 1976; Giauque et al., 1980; Saether et al., 1981; Giauque 1981.

correlating mineral phases and elemental abundance data for 280 samples of oil shale. This work revealed that more than half of the 57 elments studied correlated well with the minerals Na-feldspar and K-feldspar. Subsequent, unpublished work by these investigators showed that As, Mo, Se, and Hg correlated well with total sulfur, suggesting residence in the sulfide minerals (Giauque, 1981). Saether et al. (1981) demonstrated that F is associated with micaceous clay minerals, especially illite, in the Mahogany Zone. Other work is underway at Lawrence Berkeley Laboratory (LBL) (Giauque, 1981) to investigate the minor mineralogy of a core from the Geokinetics site near Book Cliff, Utah, and at Los Alamos National Laboratory (LANL) (Peterson, 1981) to investigate the minor mineralogy of a core from Occidental's Logan Wash site.

Elemental Composition

The elemental composition, although of interest, is not as significant as mineralogy in studying the leaching behavior of raw and spent shales. The elemental abundances in raw oil shales have been studied by a number of investigators (Poulson et al., 1977; Desborough et al., 1976; Fruchter et al., 1980; Cook, 1973; Giauque et al., 1980; Fox, 1980a). Some of this work has been summarized by Fox (1980a), Wildung and Zachara (1981), and Fox et al. (1982). These studies indicate that the major elements (concentrations greater than 1%) in oil shales of the Green River Formation are Al, Ca, Fe, K, Mg, Na, F, Ti, S, and Si. This is consistent with the major mineralogy discussed above. The environmentally important elements which occur at concentrations between 1 and about 500 ppm are Mn, V, Zn, As, Cu, Cr, Mo, Ni, Pb, Co, U, and Se. Cadmium and Hg occur at concentrations below 1 ppm in most samples.

Recent studies by Giauque et al. (1980) on 280 samples from two core holes on the Naval Oil Shale Reserve No. 1 indicate the concentration of most of the 57 elements that they studied did not vary with depth by more than a factor of three or four. However, variations of a factor of 10 or greater were observed for As, Cd, Hg, Mo, Se, B, F, H, N, and organic C. This is demonstrated by the data in Table 3-5 which summarizes elemental ranges for the two core holes studied by Giauque et al. (1980). Similar results have been obtained for a third corehole from the Geokinetics site at Book Cliff, Utah (Giauque, 1981).

Organic Composition

The organic fraction of oil shale is believed to have originated from algae and other microorganisms that lived in ancient Lake Gousite and from wind-blown or water-borne pollens and waxy spores (Bradley, 1931). This organic fraction varies from a few percent in low-grade shales to more than 40 percent in shales that yield 75 gallons of oil per ton. The elemental composition of the organic fraction is shown in Table 3-3. The empirical formula of the organic fraction has been reported as $C_{215}H_{330}O_{12}N_5S$ with a minimum formula weight of 3,200 (Smith, 1961). It is highly aliphatic, has a H/C ratio of 1.53, and consists of three fractions--kerogen, bitumen, and an inert substance.

Kerogen typically constitues 80% to 90% of the total organic matter. This material is insoluble in organic solvents and yields oil, gas, and char on pyrolysis. The structure of kerogen is not completely understood, even though it has been extensively studied (Robinson, 1976). This work suggests that kerogen exists as a complex polymeric assemblage composed of linear networks of cyclic rings of methylene groups with associated long chains and aromatic structures (Robinson, 1969, 1976; Robinson and Stanfield, 1960; Robinson and Lawlor, 1961; Schmidt-Collerus and Prien, 1976).

Bitumen, the second major organic fraction, typically constitutes about 10% of the organic material in oil shale. It is a heteroatomic polymer which is soluble in many conventional organic solvents and which also decomposes on pyrolysis. This soluble material has been fractionated into about 1% n-alkanes, 3% alkanes, 21% cyclic alkanes, 2% aromatic oils, 63% resins, and 10% pentane-insoluble material. The third fraction, which occurs in very small amounts, is an inert substance which is insoluble in organic solvents and which does not decompose on pyrolysis.

RAW SHALE LEACHATES

Leachates will be produced by the contact of rainfall and snowmelt with storage and disposal piles of raw shale. Climatic conditions and chemical, mineralogical, and geotechnical properties of the raw shale piles will determine the quantity and composition of field leachates. Because of the relatively high porosity and permeability of raw shales, most of these leachates will percolate through the piles. Precipitation and evaporation data for oil shale regions suggest that raw shale piles will slowly, and perhaps never, be saturated throughout their depth; unsaturated conditions will exist, particularly near the surface of the pile.

TABLE 3-5

Elemental Concentration Ranges for Two Core Holes From the Naval Oil Shale Reserve No. 1 (Giauque et al., 1980).[a]

	Core Hole 15/16	Core Hole 25		Core Hole 15/16	Core Hole 25
Ag	<0.7 - 1.7	<1.0 - 1.4	La	10 - 34	12 - 32
Al(%)	1.8 - 6.9	2.0 - 6.5	Lu	0.08 - 0.34	0.11 - 0.36
As	5 - 134	8 - 98	Mg(%)	1.8 - 5.8	1.9 - 5.9
Au	<0.02 - 0.4	<0.03 - 0.14	Mn	190 - 460	201 - 440
B	25 - 250	40 - 200	Mo	4 - 54	7 - 48
Ba	240 - 1230	270 - 800	N(%)	0.2 - 1.2	0.2 - 1.1
Br	<0.6 - 1.4	<0.6 - 0.8	Na(%)	0.4 - 3.1	0.4 - 3.1
C min(%)	1.9 - 7.2	2.1 - 7.2	Nd	8 - 30	9 - 25
C org(%)	3 - 35	2 - 29	Ni	11 - 32	11 - 30
Ca(%)	5 - 21	5 - 19	Pb	8 - 41	9 - 39
Cd	b	0.2 - 1.4	Rb	32 - 124	47 - 139
Ce	21 - 69	25 - 63	Sb	0.5 - 5.2	0.8 - 3.9
Cl(%)	0.05 - 0.12	0.05 - 0.09	Sc	3 - 12	4 - 10
Co	5 - 14	4 - 13	Se	0.5 - 12.3	0.5 - 3.7
Cr	18 - 60	17 - 54	Sm	1.5 - 5.0	1.7 - 5.3
Cs	0.7 - 14	2.0 - 5.9	Sn	<80 - 130	<80 - 130
Cu	11 - 63	14 - 58	Sr	260 - 1440	300 - 1120
Dy	1.1 - 3.9	1.3 - 4.9	Ta	0.24 - 0.74	0.27 - 0.77
Eu	0.3 - 1.1	0.4 - 1.0	Tb	0.15 - 0.58	0.20 - 0.73
F	200 - 3200	100 - 2500	Th	3.1 - 10.6	3.8 - 9.2
Fe(%)	1.0 - 3.5	1.1 - 3.2	Ti(%)	0.03 - 0.28	0.06 - 0.27
Ga	3 - 17	5 - 16	U	1.8 - 8.2	2.0 - 6.1
Ge	<1.1 - 2.3	<1.1 - 2.0	V	29 - 203	45 - 185
H(%)	0.3 - 4.5	0.4 - 3.8	W	<0.8 - 11	<0.9 - 3.0
Hg	0.01 - 0.50	0.03 - 0.21	Y	2 - 23	4 - 28
Hf	0.8 - 2.7	1.1 - 3.5	Yb	0.6 - 2.5	0.8 - 2.6
In	<0.1 - 0.6	0.1 - 0.3	Zn	38 - 153	41 - 111
Ir	<0.004 - 0.008	<0.005 - 0.009	Zr	13 - 73	18 - 219
K(%)	0.6 - 5.6	0.8 - 5.7			

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[a] All concentration ranges are in ppm unless otherwise indicated.

[b] Concentration range not determined.

The raw shale leaching studies completed to data are summarized in Table A-1 in the Appendix. This table indicates that the leaching characteristics of only a few samples of raw shale have been investigated. Most published work consists of preliminary screening tests (McWhorter, 1980; Jackson et al., 1975) or limited measurements made in conjunction with spent shale leaching studies (Margheim, 1975; Stollenwerk, 1980; Saether, 1980).

Investigations have been conducted on the effect of wetting and drying cycles and contact time on pH and the concentrations of TDS, F, Mo, B, As, and Se in leachates (Stollenwerk, 1980; Saether, 1980; McWhorter, 1980). Other studies have investigated the effect of saturated and unsaturated conditions on leachate composition (McWhorter, 1980). Chemical species of F, B, Mo, and As have been determined in leachates using equilibrium models (Saether, 1980; Stollenwerk, 1980) or experimental techniques (Fox, 1982a). The release mechanisms and aqueous chemistry of F have been exhaustively studied for raw shale from the Colony Mine (Saether, 1980). Other work is in progress to evaluate the effect of raw shale mineralogy on leachate composition (Peterson, 1981) and to investigate raw shale leaching under field conditions (Bates, 1981).

The major conclusion emerging from this work is that the various raw shales investigated are unique in terms of their leaching behavior. It is presently difficult to make generalizations about "raw shale", and each must be individually considered. Also, these studies indicate that dissolved salts and certain trace elements, such as F and Mo, are elevated in most raw shale leachates and may pose an environmental hazard if discharged into the environment with no treatment. This result indicates that present raw shale disposal and storage plans may be inadequate. These two significant results suggest that more work is warranted to elucidate the mechanisms of raw shale leaching and to evaluate its significance.

CHARACTERIZATION OF RAW SHALE LEACHATES

Most studies of raw shale leachates have identified and quantitated inorganic species. The chemical composition of raw shale leachates has been determined in laboratory studies for samples from the Colony Mine, the Anvil Points Mine, the USBM shaft, and Tract C-a (Stollenwerk, 1980; McWhorter, 1980; Saether, 1980; Margheim, 1975). Other work is in progress to evaluate the effect of raw shale mineralogy on leachate composition using core material from Logan Wash and Tract C-a (Peterson, 1981) and to determine the composition of raw shale leachates from field lysimeters at Tracts C-a and C-b (Bates, 1981; Rio Blanco, 1981; McWhorter, 1981b).

Very little work has been conducted on the organic species present in these leachates even though the reported concentrations of organic carbon are typically higher than in surface and in situ spent shale leachates. The author is not aware of any published analyses of organic compounds in raw shale leachates. However, some work is underway at the U.S. Geological Survey to characterize organics in leachates from the Tract C-a and C-b lysimeters (McWhorter, 1981b). Because of the absence of organic characterization data, the raw shale leachate characterization section will address only inorganics.

Elemental Composition

The range in chemical composition of raw shale leachates produced in column studies using deionized water and lysimeters of run-of-mine shale at Tracts C-a and C-b are summarized in Table 3-6. The ranges summarized from McWhorter (1980) were from column studies in which seven or more pore volumes of leachate were analyzed while those summarized from Stollenwerk (1980) are for the first pore volume of leachate analyzed in quarters. The lowest reported value from column studies (first six columns on Table 3-6) was generally obtained later in the leaching procedure, after several pore volumes (McWhorter, 1980) or in the last quarter pore volume (Stollenwerk, 1980) while the highest value was obtained early in the leaching experiments, in the first pore volume (McWhorter, 1980) or in the first one-quarter pore volume (Stollenwerk, 1980). The inverse is true for the lysimeter studies (last two columns on Table 3-6); the lowest reported value typically was obtained in early leachates while the highest reported value was obtained on the last date samples were collected (exceptions include Si). Chemical analyses of batch leaching studies with deionized water are presented in Table 3-7.

An analysis of these composition data shows that the leachate from each raw shale is distinctive for reasons not yet understood. And samples from the same mine have displayed unexpected differences in leaching behavior (Runnells and Esmaili, 1981). Work is in progress at LANL to resolve some of these issues. A single, well defined and reproducible batch test is being used to study the leaching characteristics of ten-foot segments of raw shale from two coreholes as a function of mineralogy (Peterson, 1981).

The available data indicate that most raw shale leachates have a pH between 6.8 and 8.0 with some samples reaching higher values. Jackson et al. (1975) observed pHs of 9.3 to 9.8 in a Utah raw shale leachate (Table 3-7) while McWhorter (1980) recorded pHs of 11.14 to 11.98 in R-5 and Mahogany Zone leachates, and McWhorter (1981b) reported a single pH greater than 9.0 in Tract C-b leachates. The total dissolved solids (TDS) in most raw shale leachates ranges from 100 to 10,000 mg/L with the lower values occurring after several pore volumes have passed through the column. Most raw shale leachates have lower concentrations of TDS than spent shale leachates due to the absence of relatively soluble alkaline earth oxides and soluble alkali salts produced during some retorting processes. Additionally, kerogen coats the inorganic grains, making raw shale initially hydrophobic (Saether, 1980). In general, the major cations in raw shale leachates are Ca, Mg, Na, and K, and the major anions are SO_4, HCO_3, CO_3, and Cl. The minor constituents that occur at elevated concentrations include NO_3, F, B, and Mo. Organic carbon also is elevated in raw shale leachates.

Colony Mine and Anvil Points Leachates

The most extensive published raw shale leaching studies have been conducted in laboratory investigations of material from the Anvil Points and Colony mines (Stollenwerk, 1980; Saether, 1980; Fox, 1982a; McWhorter, 1980; Runnells and Esmaili, 1981). Samples from these mines have been available for a decade or more and are from a well-defined stratigraphic region.

TABLE 3-6

Range in Composition of Raw Shale Leachates Produced in Column Studies and Lysimeters Using Deionized Water (mg/L Unless Otherwise Noted).

	Saline Zone (USBM Horse Draw Site)[a] (McWhorter, 1980)	Mahogany Zone Colony Mine[b] (McWhorter, 1980)	Mahogany Zone Anvil Points Mine[c] (Stollenwerk, 1980)	Mixture of R-5 and Mahogany Zone, Tract C-a[d] (McWhorter, 1980)	Tract C-a Composite[e] (McWhorter, 1980)	Mahogany Zone, Tract C-a[f] (Stollenwerk, 1980)	Tract C-a Run-of-Mine[g] (McWhorter, 1981b)	Tract C-b Run-of-Mine[h] (McWhorter, 1981b)	
Al	0.34 - 7.54	<0.05 - 0.75	≤0.1	0.3 - 3.53	<0.05 - 0.69	≤0.1	0.5 - 2.0	0.3 - 9.7	Al
As	<0.005	<0.005	0.19 - 0.40	<0.005	<0.005	0.01	-	-	As
B	0.24 - 43	<0.025 - 2.75	13 - 30	<0.025 - 0.59	<0.025 - 1.97	0.5 - 1.1	0.184 - 0.492	0.136 - 0.980	B
Ba	0.061 - 0.17	0.07 - 0.48	-	0.088 - 0.27	0.027 - 0.22	-	0.030 - 0.099	0.027 - 0.215	Ba
Be	<0.025	<0.025	-	<0.025	<0.025	-	<0.0005 - 0.0062	<0.0005 - 0.0038	Be
Br	-	-	0.04 - 0.07	-	-	0.02 - 0.11	-	-	Br
Ca	36 - 750	40 - 1550	3.3 - 8.6	180 - 1510	18 - 970	550 - 590	364 - 720	6.9 - 693	Ca
Cl	<1.0 - 560	1.1 - 22	5.3 - 24	1.9 - 300	0.3 - 130	1.8 - 18	52 - 412.2	4.7 - 25.8	Cl
CO_3	0.1 - 1.1	0.03 - 1.6	-	<0.1 - 346	0.3 - 0.7	-	0.01 - 0.42	1.9 - 7.4	CO_3
Cr	<0.025 - 0.68	<0.025 - 0.04	<0.01 - 0.05	0.022 - 0.034	<0.025 - 0.043	0.04 - 0.06	<0.1	<0.1 - 0.71	Cr
Cu	<0.025 - 0.30	<0.025 - 0.41	0.01 - 0.03	<0.025 - 0.69	<0.025 - 0.44	0.02 - 0.04	0.013 - 0.435	0.0049 - 0.299	Cu
EC, μmhos/cm	280 - 13,000	240 - 5400	-	1900 - 37,000	125 - 8200	-	3060 - 22,800	2000 - 6590	EC μmhos/cm
F	9.5 - 75	4.0 - 7.2	59 - 115	0.8 - 65	<0.5 - 3.0	2.0 - 4.3	2.5 - 22.0	2.6 - 23.0	F
Fe	0.01 - 1.8	<0.03 - 0.89	0.04 - 0.30	<0.1	<0.1	0.04 - 0.08	<0.001 - 0.004	<0.001 - 0.24	Fe
HCO_3	83.1 - 321	50 - 558	1800 - 3800	3.0 - 403	82 - 1026	210 - 500	56 - 119	228 - 1100	HCO_3
Hg	<0.0001 - 0.0035	<0.0005	-	<0.0001	<0.0001	-	-	-	Hg
K	1.1 - 22	1.7 - 59	7.0 - 15	8.2 - 640	0.4 - 34	12 - 21	5.9 - 12	1.1 - 9.0	K
Li	0.02 - 3.1	0.02 - 0.151	-	0.02 - 0.11	<0.02 - 0.79	-	0.059 - 0.217	0.037 - 0.279	Li
Mg	6.7 - 1050	5.5 - 140	3.3 - 12	0.675 - 108	4.9 - 820	360 - 970	225 - 11,400	4.7 - 270	Mg
Mn	0.075 - 3.2	0.074 - 2.74	≤0.01	<0.05 - 0.35	<0.05 - 0.40	0.41 - 0.60	0.086 - 3.06	0.0021 - 0.160	Mn
Mo	0.09 - 0.87	0.09 - 0.65	7.4 - 31	0.10 - 5.18	0.10 - 2.2	0.98 - 2.1	<0.05 - 4.7	0.9 - 11.3	Mo
Na	<25 - 1430	5.8 - 145	930 - 2400	27 - 7710	4.3 - 1240	140 - 490	376 - 1824	727 - 1760	Na
NH_4	-	-	1.9 - 4.6	-	-	7.3 - 14	1.19 - 20.2	0.36 - 4.0	NH_4
Ni	<0.025 - 0.60	<0.05 - 0.10	0.01 - 0.04	0.047 - 0.085	<0.05 - 0.16	0.14 - 0.30	0.08 - 1.5	<0.05 - 0.91	Ni
NO_3	<1.25 - 40	0.9 - 25	<1.9	4 - 172	<0.5 - 140	20 - 80	370 - 2118	57.6 - 380	NO_3
NO_2	-	-	<0.2	-	-	0.1 - 0.2	-	-	NO_2
Pb	<0.04 - 1.9	<0.05 - 0.64	<0.01 - 0.03	<0.05 - 0.83	<0.05 - 0.77	<0.01	<0.3 - 20.6	<0.3 - 2.4	Pb
PO_4	-	-	0.15 - 0.45	-	-	0.09 - 0.18	<0.1 - 3.8	<0.05 - <0.1	PO_4
Rb	-	-	0.01 - 0.02	-	-	0.04 - 0.10	-	-	Rb
Se	<0.01	<0.01	0.01 - 0.02	<0.005	<0.005	0.01 - 0.05	-	-	Se
Si	1.65 - 9.7	2.12 - 10.58	6.1 - 7.5	1.2 - 23.4	5.8 - 19.6	13 - 14	1.7 - 5.3	2.7 - 29	Si
Sn	<0.025 - 1.28	0.12 - 0.67	0.01 - 0.02	-	-	<0.02	-	-	Sn
SCN	-	-	<10	-	-	<10	-	-	SCN
SO_4	20 - 5700	28 - 5150	700 - 1800	5 - 6600	7.9 - 6100	2400 - 4900	1500 - 36,920	490 - 3800	SO_4
S_2O_3	-	-	<10	-	-	<10	-	-	S_2O_3
S_4O_6	-	-	<10	-	-	<10	-	-	S_4O_6
Sr	-	-	0.08 - 0.26	-	-	8.0 - 9.1	4.0 - 10.8	0.27 - 16.0	Sr
TDS	70 - 13,300	110 - 7160	3600 - 8700	610 - 30,130	164 - 9450	3700 - 7600	8910 - 53,640	1960 - 6830	TDS
TOC	-	-	100 - 370	-	-	13 - 52	-	-	TOC
U	-	-	0.01 - 0.02	-	-	0.05 - 0.30	-	-	U
Zn	0.01 - 6.8	<0.02 - 0.68	0.03 - 0.08	<0.01 - 0.09	<0.02 - 1.5	0.03 - 0.16	0.02 - 0.401	0.02 - 0.455	Zn
Zr	-	-	0.02 - 0.19	-	-	<0.08 - 0.18	-	-	Zr
pH, units	6.8 - 8.06	7.06 - 8.18	8.4 - 8.5	6.93 - 11.98	7.03 - 7.99	7.3 - 7.4	6.49 - 9.00	7.66 - 9.44	pH, units
Type of Exp.	Column	Column	Column	Column	Column	Column	Lysimeter	Lysimeter	Type of Exp.
Particle Diam (D_{50})	5 mm	6.7 mm	-	4.2 mm	3.5 mm	-	Run of Mine	Run of Mine	Particle Diam (D_{50})
Solid-to-Liquid Ratio	5.5 g/mL	7.5 g/mL	4.5 g/mL	3.4 g/mL	4.3 g/mL	3.4 g/mL	-	-	Solid-to-Liquid Ratio
Residence Time	19-74 hrs	90-103 hrs	+46 days	28-108 hrs	23-67 hrs	+46 days		-	Residence Time

[a] Sample from a drift at 4208 feet below mean sea level which had been stockpiled outside for about 6 weeks prior to collection. Leaching was conducted in a PVC column 15 cm dia. and 107 cm long, at a rate of 1.3-4.7 mL/min under saturated and unsaturated conditions. Columns run for 9 to 15 pore volumes (PV = 5400 mL).

[b] Sample from a stockpile of -½ in. material that was mined about 6 yrs. prior to collection; sample was collected well below pile surface. Leaching was conducted in a PVC column, 15 cm dia. and 107 cm long, at a rate of 0.7-0.8 mL/min under saturated conditions. Column run for 11 to 13 pore volumes (PV = 4290 mL).

[c] Sample from a fresh stockpile of fines too small for Paraho retort feed. Leaching was conducted in a borosilicate glass column, 8.5 cm dia. and 30 cm long. Column was equilibrated for 46 days, and one pore volume (PV = 466 mL) was collected and analyzed in quarters.

[d] Sample is a mixture of shale from the R-5 and Mahogany Zone on Tract C-a. Leaching was conducted in a PVC column, 15 cm dia. and 107 cm long, at a rate of 1.2-4.5 mL/min under saturated and unsaturated conditions. Columns run for 7-15 pore volumes (PV = 7463 mL).

[e] Sample is a mixture of trimmings from the service shaft at Tract C-a. Leaching was conducted in a PVC column, 15 cm dia. and 107 cm long, at a rate of 1.6-4.6 mL/min under saturated and unsaturated conditions. Columns were run for 10-20 pore volumes (PV = 6344 mL).

[f] Sample collected from fresh disposal pile of raw shale from mine works. Leaching was conducted in a borosilicate glass column, 8.5 cm dia. and 40 cm long. Column was equilibrated for 46 days, and one pore volume (PV = 650 mL) was collected and analyzed in quarters.

[g] Range for samples collected from 8/80 - 5/81 from 5-ft and 15-ft collectors or lysimeter.

[h] Range for samples collected from 3/80 - 6/81 from 5-ft, 10-ft, 15-ft, and 20-ft collectors or lysimeter.

TABLE 3-7

Summary of Batch Leaching Experiments Using Raw Shale and Deionized Water (mg/L Unless Otherwise Noted).

	Mahogany Zone, Anvil Points Mine (Margheim, 1975)	Mahogany Zone, Colony Mine[a] (Runnells and Esmaili, 1981)	Mahogany Zone, Colony Mine[a] (Stollenwerk, 1980)	Utah shale (Jackson et al., 1975)
As	-[b]	<0.2	0.02	-
B	-	1.6	2.8	0.019 - 0.057
Ca	10	144	-	5.2 - 6.7
Cl	2.2	6.0	-	3.6 - 4.5
CO_3	-	-	-	11 - 15
F	-	8	18	0.2 - 0.35
HCO_3	75	-	-	37
K	24	10	-	0.6 - 0.8
Mo	-	0.22	1.1	-
Mg	1.0	78	-	1.1 - 1.6
Na	48	120	-	1.4 - 20
NO_3	-	3	-	0.2 - 2.0
Se	-	<0.3	0.07	-
Si	-	-	-	0.4 - 1.3
SO_4	79	605	-	1.2 - 11
TDS	277	1130	1500	61 - 113
TOC	-	76	-	1
pH, units	8.15	7.7	7.2	9.3 - 9.8
Type of experiment	Blender	Shaker	Shaker	Blender
Particle diameter	-0.25 mm	-[b]	-0.15 mm	0 - 0.4 cm 2.4 - 47 cm
Solid-to-liquid ratio	0.10 gm/mL	0.40 gm/mL	0.40 gm/mL	0.10 gm/mL
Residence time	5 min	17 days	41 days	5 min
Sample filtered	yes	yes	yes	yes

[a] The Colony Mine sample analyzed by Runnells and Esmaili is a fresh sample collected in June 1980; the sample analyzed by Stollenwerk (1980) was collected by Wildeman (1977) and crushed to -65 mesh.

[b] Not reported.

The major ions in raw shale leachates from the Colony Mine are Ca, Mg, Na, HCO_3, and SO_4 (McWhorter, 1980; Runnells and Esmaili, 1981) while the major ions in raw shale leachates from the Anvil Points Mine are Na, SO_4, and HCO_3 (Margheim, 1975; Stollenwerk, 1980); Ca and Mg are notably reduced in Anvil Points leachates compared to Colony Mine leachates. This is undoubtedly related to raw shale mineralogy, and Stollenwerk (1980) hypothesized that the high Na and HCO_3 in leachate may be due to the presence of nahcolite and/or dawsonite in the Anvil Points sample.

The trace elements which are sufficiently elevated to be of environmental concern (greater than 0.1 mg/L) in initial leachates from Colony Mine raw shale are B, Cu, F, Li, Mn, Mo, Sn, and Zn while in Anvil Points raw shale, they are B, F, Mo, and As. Arsenic, B, and F are significantly higher and Cu, Ni, Pb, and Zn are significantly lower in Anvil Points leachates than in Colony Mine leachates. Mineralogical controls responsible for these variable results have not been investigated except for F (Saether, 1980). Samples from the Colony Mine have high NO_3 levels (0.9-25 mg/L) while NO_3 in Anvil Points samples was uniquely low among raw shales studied (Table 3-6). Samples from both mines had high organic carbon concentrations. These reported organic carbon levels are higher than most values reported for spent shales (see Table 4-5). No work has been conducted to determine the composition of this organic carbon.

In Situ Development Site Leachates

Other work has been conducted (McWhorter, 1980; Stollenwerk, 1980) or is in progress (Bates, 1981; Peterson, 1981; Rio Blanco, 1981; McWhorter, 1981b) to characterize leachates from Logan Wash, Tract C-a, and Tract C-b raw shales. Stollenwerk (1980) and McWhorter (1980) have used laboratory columns to study leachates from several stratigraphically mixed samples of raw shale from Tract C-a. These studies indicate that there are some important differences among the three samples investigated but that, in general, the major ions in all three are Ca, Mg, Na, HCO_3, SO_4, and Cl. The mixture of R-5 and Mahogany Zone material reported by McWhorter (1980) had an unusually high pH and high concentrations of TDS, Na, Al, and K.

Work also has been initiated to characterize raw shale leachates from Tract C-a and C-b raw shales using field lysimeters (Bates, 1981). The purpose of these studies is to evaluate the importance of such factors as percolation rates, wetting and drying cycles, and other weathering factors in the field. A single lysimeter with leachate collectors at the 5-, 10-, and 15-foot depths was constructed in mid-June 1980 at the run-of-mine raw shale stockpile on Tract C-a. Three other raw shale lysimeter studies, with collectors at the 10-, 15- and 20-foot depths, have been constructed on Tract C-b (Bates, 1981). Only preliminary, unpublished data are available from these sites, and data interpretations are subject to change. Preliminary analyses from these lysimeters are summarized in the last two columns of Table 3-6. It is difficult to directly compare these analyses with those from laboratory column studies because the field samples contain groundwaters that drain, they are leached with precipitation which is different from distilled water used in the laboratory, and the lysimeter samples are leached under unsaturated conditions. Composition of precipitation, which was not reported in the McWhorter (1981b) study, may be important in determining leachate quality. Evidence has been presented recently (Harte et al., 1982) that acid precipitation occurs on the western slope of the high Colorado Rockies. Such acidic precipitation would affect the solubility of minerals from raw shale.

The initial leachates from the C-a and C-b lysimeters were believed to represent drainage of waters contained in the raw shale at the time of placement (i.e., groundwater) (McWhorter, 1981b). No significant leachate volume was produced in any of the collectors until the spring of 1981. The preliminary data reveal a gradual increase in concentration of many of the parameters studied (e.g., EC, TDS, Cl, NO_3, SO_4). Notable exceptions are Si and Mo. A comparison of the data from the C-a lysimeter with that from the C-b lysimeter reveals that Tract C-a raw shale leachates have much higher concentrations of dissolved salts (TDS, EC) and of Cl, Mg, NO_3, and SO_4 than C-b leachates. Most toxic trace element concentrations are low with the exception of Al, Cu, F, Mn, Mo, Ni, and Pb at Tract C-a and Al, Cu, F, Ni, and Mo at Tract C-b.

Peterson (1981) is presently studying the relationship between raw shale mineralogy and leachate composition using a core from Occidental's Logan Wash site between retorts 7 and 8 and a second core from tract C-a. Preliminary results from the 1000-foot Logan Wash core indicate that there are at least two distinct zones. Raw shale from the first zone, which extends from 450 feet below the surface down for 250 feet, is relatively insoluble and is characterized by leachates with high concentrations of Ca, Mg, Sr, and SO_4 and low concentrations of most trace elements. The second zone, which includes the retorting horizon, includes the next 300 feet of core. The raw shale in this zone is more soluble than in the first zone, and its leachate is characterized by high concentrations of Na, HCO_3, and certain trace elements including As, Mo, B, Mo, F, and V. Preliminary mineralogic analyses suggest that these marked differences are at least partly due to differences in clay mineralogy.

Chemical Species

The chemical species in leachates from raw shales have been investigated using a computer equilibrium model (Saether, 1980; Stollenwerk, 1980) and by experimental techniques (Fox, 1982a). Saether (1980) and Stollenwerk (1980) used a modified version (Runnells and Lindberg, 1980) of the USGS computer program (Truesdell and Jones, 1974) to calculate the equilibrium distribution of inorganic aqueous species. They studied the first pore volume of leachate from columns packed with Anvil Points and Tract C-a raw shale (Table 3-6). The results of Stollenwerk's (1980) analyses for Ca, Mg, Na, K, Cl, SO_4, HCO_3, F, B, and Mo are summarized in Table 3-8. This data reveals that leachate from the Anvil Points sample contains predominantly Na, HCO_3 and SO_4. Stollenwerk (1980) hypothesized that the elevated concentration of Na and HCO_3 in the Anvil Points material were from nahcolite and/or dawsonite in this raw shale.

These analyses indicate that more than 99% of the dissolved Mo exists as the free molybdate ion MoO_4^{-2} and the concentration of Mo in raw shale leachate is probably controlled by the solubility of $CaMoO_4$. The dominant aqueous species of B in raw shale leachates are $B(OH)_3^0$ and $B(OH)_4^-$, with the

TABLE 3-8

Chemical Species Present in First Pore Volume Leachates of Paraho Raw Shale (Anvil Points Mine) and of a Raw Shale Composite From Tract C-a Computed Using WATEQFC, a Chemical Equilibrium Model (Stollenwerk, 1980).

Constituent	Concentration (mm/L)[a]	
	Anvil Points	Tract C-a Composite
Cl^-	0.68	0.51
$NaCl^o$	0.001	0.001
(Total Cl)	(0.68)	(0.51)
SO_4^{2-}	16	29
$NaSO_4^-$	2.9	1.0
$MgSO_4^o$	0.09	15
$CaSO_4^o$	0.05	5.5
$NH_4SO_4^-$	0.02	0.09
KSO_4^-	0.01	0.03
(Total SO_4)	(19)	(51)
HCO_3^-	56	7.1
$NaHCO_3^o$	1.8	0.05
CO_3^{2-}	1.4	0.02
$NaCO_3^-$	1.0	0.002
$MgHCO_3^+$	0.06	0.76
$CaHCO_3^+$	0.02	0.21
$H_2CO_3^o$	0.38	0.59
$MgCO_3^o$	0.05	0.04
$CaCO_3^o$	0.03	0.02
(Total HCO_3 + CO_3)	(64)	(8.3)
Ca^{2+}	0.11	8.1
$CaSO_4^o$	0.05	5.5
$CaCO_3^o$	0.03	0.02
$CaHCO_3^+$	0.02	0.21
CaF^+	0.002	0.004
(Total Ca)	(0.22)	(14)

Constituent	Concentration (mm/L)[a]	
	Anvil Points	Tract C-a Composite
Mg^{2+}	0.25	24
$MgSO_4^o$	0.09	15
$MgHCO_3^+$	0.06	0.76
$MgCO_3^o$	0.05	0.04
MgF^+	0.04	0.08
(Total Mg)	(0.50)	(40)
Na^+	99	20
$NaSO_4^-$	2.9	1.0
$NaHCO_3^o$	1.8	0.05
$NaCO_3^-$	0.95	0.002
NaF^o	0.20	0.001
$NaCl^o$	0.001	0.001
(Total Na)	(105)	(22)
K^+	0.36	0.51
KSO_4^-	0.01	0.03
(Total K)	(0.38)	(0.54)
F^-	5.9	0.14
NaF^o	0.20	0.001
MgF^+	0.04	0.08
CaF^+	0.002	0.004
(Total F)	(6.1)	(0.23)
$B(OH)_3^o$	2.3	0.10
$B(OH)_4^-$	0.45	0.002
(Total B)	(2.8)	(0.10)
MoO_4^{2-}	0.33	0.02
(Total Mo)	(0.33)	(0.02)

[a] Millimoles/L

ratio controlled by pH. The predominance of the neutrally charged species suggests that B may not be sorbed by natural geological material on release from storage and disposal piles. The free fluoride anion, F^-, is the predominant dissolved species in raw shale leachates. Important F complexes are formed with Na, Mg, and Ca if these are present in sufficient concentrations. The concentration of F in leachates was hypothesized to be controlled by fluorite, CaF_2. Saether (1980) verified the equilibrium F distribution calculated by the computer program for a Paraho spent shale leachate by using synthetic ion exchange resins.

In other work, Fox (1982a) identified the inorganic arsenic and organoarsenic species present in Anvil Points raw shale leachate using a high performance liquid chromatograph automatically coupled to a graphite furnace atomic absorption detector. The molecular forms of arsenic in this sample were tentatively identified as arsenite, methylarsonic acid, and arsenate. The presence of arsenite, which is a suspect carcinogen, should be verified.

RAW SHALE LEACHING MECHANISMS

The leaching of inorganic and organic material from raw shale is a complex physico-chemical process that is biologically mediated and which depends on a large number of variables. Some of the more important leaching variables include raw shale composition (mineralogy, moisture content); disposal procedures (water sprays, face slope); and climate (wet-dry cycles, precipitation volume, frequency, and quality). These primary variables determine other secondary variables such as particle size, permeability, solid-to-liquid ratio, and redox conditions which drive the underlying physical, chemical, and biological interactions of leaching.

Researchers have studied the effect of some of these variables on raw shale leachate composition. However, coverage is rather incomplete at this point, and considerable additional work is required to understand the controlling leaching mechanisms and to predict environmental impacts. More research has been conducted on the related problem of leaching of surface and in situ spent shales, and the reader is referred to those sections for additional information on potentially important leaching mechanisms.

We will review raw shale leaching studies that have addressed mechanistic aspects, organizing the discussion by variables. A similar organization is used in subsequent chapters on surface and in situ spent shale leachates.

Most raw shale leaching research has focused on the environmentally important elements F, B, Mo, As, and Se in raw shales from Anvil Points, the Colony Mine, and Tract C-a. This work has revealed that the concentration of most elements decreases rapidly, gradually leveling off to low values. The concentration of many elements recover following successive periods of wetting and drying. Raw shale mineralogy probably is the dominant factor that determines leachate composition, and clay mineralogy may play an important role.

Effect of Raw Shale Mineralogy on Leachate Composition

The composition of leachate ultimately depends on the mineralogy of the raw shale. Very little information is available on the relationship between mineralogy and raw shale leachate composition, although this topic has been studied for spent shale leachates.

Preliminary work by several investigatory suggests that clay mineralogy may play an important role in the leaching behavior of raw shales. These authegenic materials may have been trace element scavengers in ancient Lake Gousite. Sorbed species would provide a large and readily leached reservoir of certain elements. Saether (1980) demonstrated that Colony Mine raw shale releases F in a nearly linear proportion to the percent solid in the solution. This suggests that desorption from the surface of the oil shale is occurring. Since F is associated principally with clay minerals, especially illite, in the Mahogany Zone (Saether et al., 1981), this suggests that desorption from clays is probably responsible for the observed leaching behavior of F. Peterson (1981), in other work, has observed elevated concentrations of As, B, Mo, F, and V in leachates from zones with mixed-layer clay minerals. These leachates also contain high particulate concentrations, and illite has been identified in the particulate phase.

Effect of Wet-Dry Cycles on Leachate Composition

The near surface environment of raw shale piles will be subject to periods of wetting and drying due to the unique climatic conditions existing in the oil shale region. Repeated infiltrations of rainfall, snowmelt, and dust control sprays followed by evaporation likely will occur. The effect of successive periods of wetting and drying has been investigated by both McWhorter (1980) and by Stollenwerk (1980). McWhorter investigated the wet-dry cycle for USBM and Colony Mine raw shales in column studies. The columns were run under saturated conditions, drained under gravity, and left in an aerated condition for several weeks. They were then re-leached. The results of these studies for EC are presented in Figure 3-3. The electrical conductivity from the second run almost completely recovers to its original value and subsequently declines at about the same rate for both shales. Similar behavior was noted for many other elements in these studies. Some elements exceed the initial values from the first column study (B, Ca, Mg, Na).

Stollenwerk (1980) also studied the wet-dry phenomenon for shales from Anvil Points and the Colony Mine. He successively batch leached raw shale under saturated conditions and dried it under a heat lamp at 40 to 50 C up to 20, 50, 100, and 150 times. Following the final drying, the shale was packed into columns, saturated, equilibrated for 10 days, and leached. His studies indicated that the concentration of TDS and Se in the first pore volume increased by a factor of two or more following 50 wet-dry cycles. The concentrations of B and F increased dramatically in both samples following 50 cycles, while the pH and concentrations of Mo and As decreased in the Anvil Points sample and remained constant in Colony Mine shale.

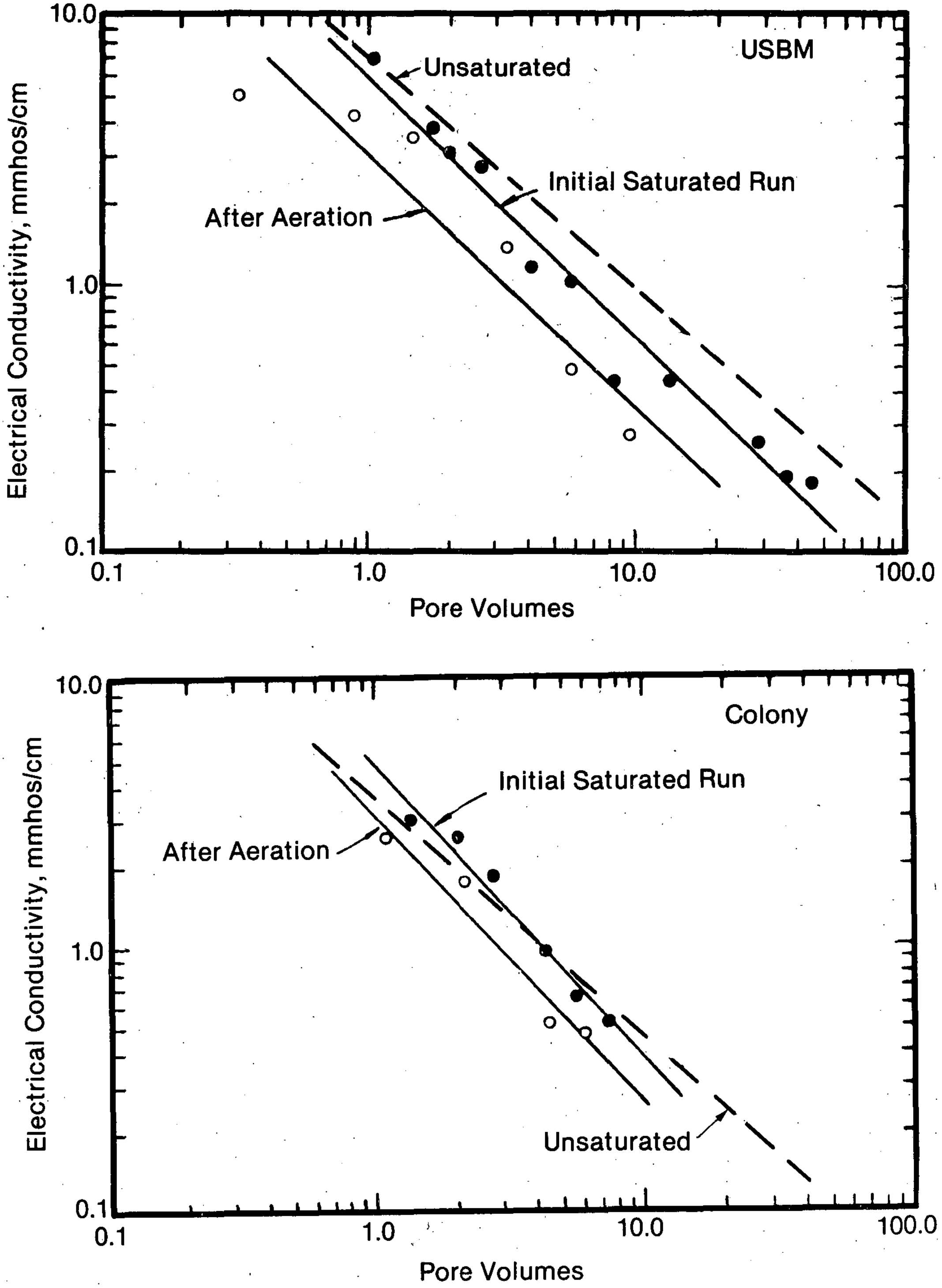

Figure 3-3. Leaching characteristics of USBM and Colony raw shale (modified from McWhorter 1980).

The decrease in concentration in successive pore volumes and the near recovery of most elements following wetting and drying has been attributed, in part, to the bimodal porosity present in raw (and spent) shale materials (McWhorter, 1981a). Piles of raw shale will have a macropore space from voids formed by the contact of shale fragments. Individual shale particles also have micropores. (These micropores are probably important in the capillary retention of water. They probably remain saturated, and soluble salts in these pores slowly migrate outward by chemical diffusion). McWhorter (1981a) has hypothesized that this bimodal property of raw shale plays an important role in its leaching characteristics.

Effect of Equilibrium Time on Leachate Composition

The effect of equilibration time on leachate composition was evaluated in other studies by Stollenwerk (1980). He filled his smaller columns with shale and saturated them for varying periods of time (0.3 to 18 months) prior to leaching. He then analyzed the first pore volume in thirds for TDS, pH, Mo, B, F, As, and Se. These studies showed that contact time between the water and shale prior to water movement has a significant effect on the composition of the first pore volume. There was no change in pH or B concentration in leachates from Anvil Points or Colony Mine raw shale for equilibration times up to 18 months. However, the concentration of TDS increased for both samples while the concentration of Mo, F, As, and Se decreased with increasing equilibration time.

Effect of Pore Volume on Leachate Composition

Investigators of the leaching behavior of both raw and spent shales have noted a rapid exponential drop in the concentration of most elements over the first few pore volumes, followed by an approach toward some lower baseline concentration. This behavior has been attributed to the rinsing out of readily soluble salts on or near the surface of the oil shale (Stollenwerk, 1980; McWhorter, 1980). After these salts are removed, slow dissolution of less soluble material (Stollenwerk, 1980) or pore diffusion of salts from the interior of the particles (McWhorter, 1981; Amy, 1978; Hall, 1982) become the controlling factor.

Stollenwerk (1980), in column experiments using Colony Mine and Anvil Points raw shale, observed that the concentration of TDS, B, and Mo decreased rapidly with increasing numbers of pore volumes. The pH remained relatively uniform throughout 20 pore volumes while the concentration of F remained high and/or increased. This behavior is summarized in Figure 3-4. Stollenwerk (1980) also noted that the slope of the straight line portion of the leaching curves for TDS, Mo, and B for the two raw shales he studied were very similar, suggesting that the same mechanism, the release of soluble salts, controls the leachate concentration of these elements.

Stollenwerk (1980) also conducted a detailed study of the variation of a large number of elements in the first pore volume of leachate using a larger column. This work showed that all constituents measured (Table 3-6) decreased across the first pore volume except Ca and Si, which remained constant, perhaps reflecting their presence in a less soluble state.

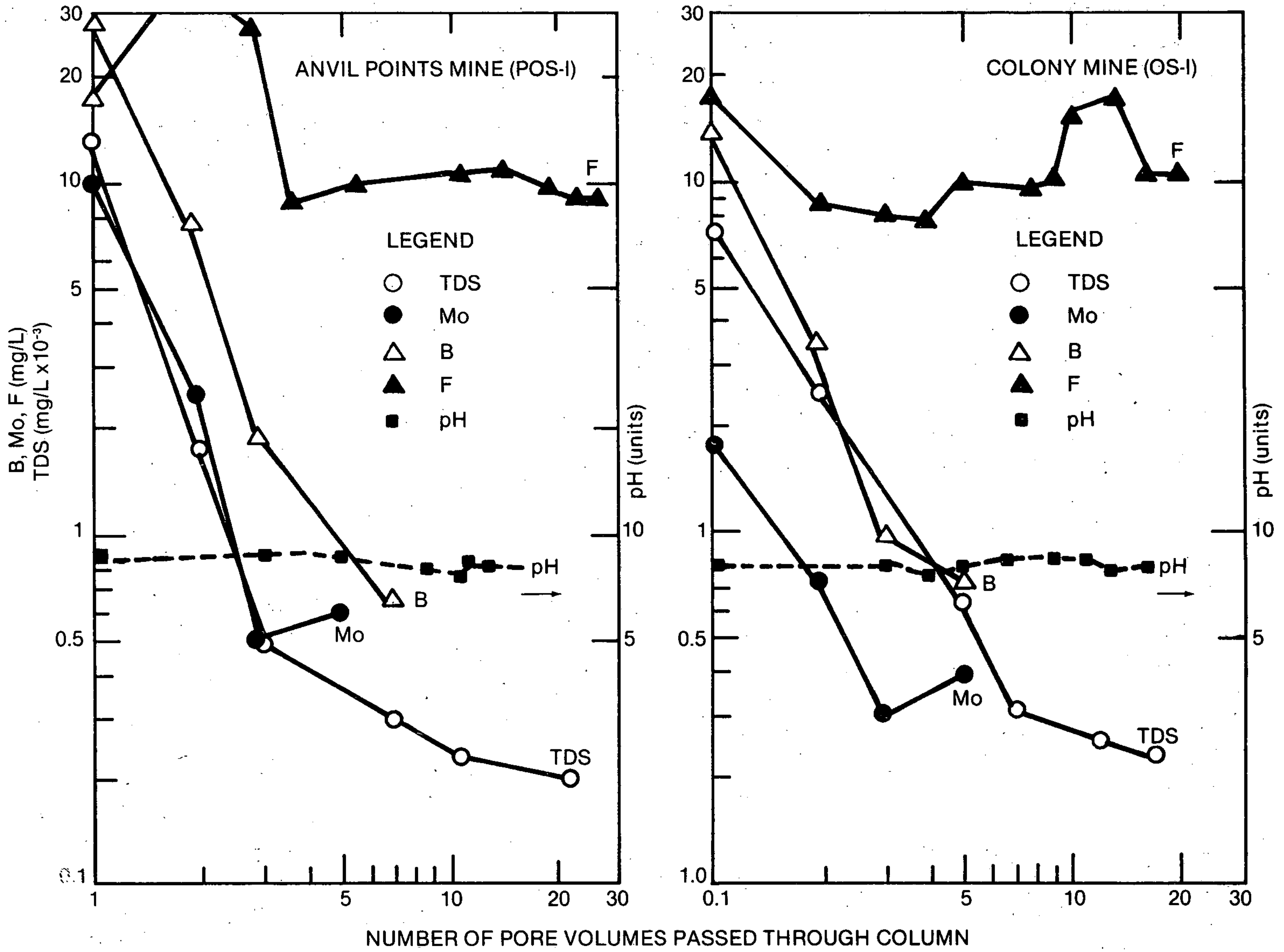

Figure 3-4. Effective pore volume on the concentration of TDS, B, F, and Mo and on pH of leachates from Anvil Points and Colony raw shales (Stollenwerk, 1980).

McWhorter (1980) also investigated the effect of pore volume on leachate composition. The details of his experiments are recorded in Table 3-6 and its footnotes. His work included analyses for four separate samples of oil shale and for additional elements not considered by Stollenwerk (1980). An analysis of McWhorter's (1980) original data indicates that all elements studied decreased significantly with increasing pore volume except Al, CO_3, Ba, and F in USBM raw shale; Ba, CO_3, Mn, and Si in Colony raw shale; and Al, Ba, and CO_3 in R-5 Mahogany Zone raw shale. The concentration of these elements (viz., Al, Ba, CO_3, F, Mn, and Si) remained relatively constant and/or increased with successive pore volumes. This behavior, also noted by Stollenwerk (1980) for F, suggests that there is a large soluble reservoir of these elements that is not readily depleted in 20 pore volumes or more and which is capable of replenishing and restoring these elements to percolating waters (Stollenwerk, 1980). This behavior has major implications for any reclamation plan which includes the "rinsing out" of soluble materials from shale wastes. While most constituents apparently can be rinsed out, others, such as F, Al, and Ba, are not.

Effect of Saturation on Leachate Composition

McWhorter (1980) also conducted experiments to determine if the state of saturation of raw shale waste was an important variable. In these column studies, he controlled the flow of water so that the major portion of the column was unsaturated. This work, which is preliminary in nature and has not been completely analyzed, indicates that the rate of leaching for electrical conductivity (see Figure 3-3) is practically the same for saturated and unsaturated conditions.

ENVIRONMENTAL TRANSPORT AND EFFECTS

Runoff and percolation from raw shale piles may reach local surface and groundwaters. As shown in Figure 1-1, percolation or mine drainage waters may move through underlying geologic materials and eventually reach alluvial and bedrock aquifers. Surface runoff, if not evaporated or recycled, may reach local streams.

The environmental transport of raw shale leachates in the extra-pile environment has not been studied. However, related investigations have been conducted for spent shale leachates, and the reader is referred to Chapters 4 and 5 for information on surface and in situ leachate transport.

Leachates released into the environment or stored and used on site may pose a health hazard or threat to existing water users. Discharges may degrade local water quality. Leachates stored behind catchment dams may be inadvertently used by waterflow or wildlife, or accidental worker contact may occur.

Two investigations have been conducted on the aquatic toxicity of raw shale leachates. Cleave et al. (1979-1980) used batch bioassays to study the effect of raw shale leachates on the productivity of freshwater algae indigenous to Lake Powell. They found that raw shale leachate stimulated the growth of their test alga, Scenedesmus, and that spent shale leachates were more biostimulatory than raw shale leachates. These investigators concluded that Colorado River salinity levels from leachates probably never would reach high enough levels to inhibit algal growth in Lake Powell, but that leachates might be biostimulatory to the algae there and may affect algal species composition.

In other work, Bergman and Meyer (1982) investigated the acute toxicity of raw shale leachates from McWhorter's (1981b) lysimeters located at Tracts C-a and C-b. They conducted 24-hr, 48-hr, 96-hr, and 120-hr tests using *Daphnia magna* and fathead minnows. They found that most raw shale leachates from Tract C-b were nontoxic to both test species. Only one sample of Tract C-b combined depth leachates had an LC 50 of less than 100% (48-hr LC 50 for *Daphnia* was 74%). However, four of the five Tract C-a raw shale leachates were toxic to both species. The LC 50 values for these four ranged from 13% to 71%, and *Daphnia* always was more sensitive than fathead minnows. The single non-toxic Tract C-a leachate contained large amounts of mine water which was displaced by low-salinity snowmelt. These investigators concluded that much of the toxicity was caused by high salinity (see Table 3-6) which produced osmotic stress. LC 50 values less than 100% usually occurred when conductivities exceeded 7000 to 8000 µmhos/cm. All of the fathead minnow acute toxicity could be explained by high salt concentrations while high salt concentrations contributed to, but did not completely explain, the observed toxicity to *Daphnia*.

Chapter 4

SURFACE SPENT SHALE

Surface retorting of oil shale requires permanent disposal of large quantities of spent shale. A 100,000 BPD plant will generate about 150,000 TPD or 125,000 cubic yards of this material. For 90% on-stream time and a 20+ year plant life, this quantity of shale will fill an area about one mile square to a depth of 1000 feet. These vast quantities of spent shale may be leached by rainfall and snowmelt or be eroded if disposed of on the surface (Routson et al., 1979). Or they may be leached by groundwater if backfilled into mines.

The handling and disposal of this vast quantity of material represents the largest solids handling and disposal operation ever attempted. Surface spent shale disposal has long been the focal point of environmental criticism of surface oil shale retorting and was a contributing factor to its slow down and the recent intensive investigations of in situ processing methods.

The next section will identify and discuss the methods of spent shale disposal at some proposed retorting sites. Subsequent sections will review and assess research completed on spent shale leaching. Chapter 7 will use this information as a basis for identifying future research needs and priorities.

SURFACE SPENT SHALE DISPOSAL PROCEDURES

Proper evaluation of spent shale leaching in modeling and laboratory studies requires a clear understanding of proposed disposal plans. Unfortunately, there is little information in the public domain on spent shale disposal plans, and a full-scale pile is yet to be built. Therefore, any discussion at this time is necessarily incomplete and subject to revision as the industry develops.

Most of the information which is in the public domain is in detailed development plans (DDPs), environmental impact statements (EISs), and environmental permits (C-b Shale Oil Project, 1976; Rio Blanco 1976, 1981; USDI 1975, 1979; White River Shale Project, 1981; Union 1979a, 1979b). Many of these plans presently are not being pursued, or the information in them is out of date. The most detailed and complete information is available on the Colony TOSCO II and the Long Ridge Union B experimental programs. Therefore, many of the remarks that follow are related to these two projects.

Some of the industry proposals for spent shale disposal are summarized in Table 4-1. Most active developments, with the exception of the Superior project, anticipate the disposal of their spent shale in local canyons or land depressions near their retorting site. A review of Table 4-1 indicates

TABLE 4-1

A Summary of Some Proposed Spent Shale Disposal Plans.

Location/Process (reference)	Commercial Production (BPD)[b]	Spent Shale Production (TPD)[b]	Total Amount of Material Disposed of (area covered)[b]	Spent Shale Treatment Prior to Disposal	Spent Shale Pile Characteristics[b]	Drainage Facilities
Tract C-b TOSCO II with room-and-pillar mining (C-b Shale Oil Project, 1976)	66,000	54,000	370 MT (1000-2000 acres)	• ROTARY DRUM COOLER Cooled to 200 F and dry-weight basis moisture content of 14%.	CROSS-VALLEY FILL Shale placed in 18-in. layers and compacted to an interior density of 85 pcf and an exterior density of 95 pcf. Field moisture content will be 13%	Unknown
Tract C-a TOSCO II and gas combustion retorting with open-pit mining (Rio Blanco, 1976)	55,800	160,000	1970.8 MT[a] (3650 acres)[a]	• TOSCO: ROTARY TUBE COOLER • Gas Combustion: MECHANICAL VIBRATING CONVEYORS Cooled to 200 F and dry-weight basis moisture content of 14% using scrubber foam, stripped foul water, plant area runoff, and process water.	CROSS-VALLEY FILL Shale will be placed in layers; interior 80% will be compacted to 85 pcf and exterior 20% to 90 pcf. The pile will be completely enclosed with overburden. Subore and overburden will be disposed of in same pile.	Unknown
Tract C-a Lurgi with open-pit mining (Rio Blanco, 1981)	2,230	3,500	3 MT (62 acres)	• SCREW MIXER or ROTARY DRUM Moisturized to 17.5% with high TDS water, treated process water, and mine water.	SURFACE PILE Mesa pile selected to facilitate experimentation. Pile to be contained by rock berms constructed of overburden. In-place density will be 65 pcf.	Runoff will be evaporated; percolation will be collected. Designed for 100-yr, 24-hr storm (2.6 in).
Colony/Dow West TOSCO II with room-and-pillar mining (USDI, 1975)	47,000	53,200	404.4 MT[a] (800 acres)[a]	• ROTARY DRUM COOLER Cooled to 200 F and moisture content of 14%.	CROSS-VALLEY FILL Shale placed in 18-in layers and compacted to an interior density of 85 pcf and an exterior density of 95 pcf. Field moisture will be 13%. Codisposal of all other solid wastes.	Runoff will be reused and/or evaporated. Designed for maximum probable storm of 6.5 in/hr.
Piceance Creek Basin Superior with room-and-pillar mining (USDI, 1979)	11,600	13,950	Unknown	• Unknown	SLURRY BACKFILL Spent shale, sludge, and dust will be moisturized to 50% with process water, mine water, etc. and backfilled into room-and-pillar mine.	Underground drainage will be collected and reused in slurrying.
Tracts U-a/U-b Superior, Union B, and TOSCO II with room-and-pillar mining (White River Shale Project, 1981)	106,300	149,800	720 MCY	• Superior & Union: WATER BATH QUENCH • TOSCO: ROTARY DRUM	CROSS-VALLEY FILL	Runoff will be used for dust control and compaction and/or evaporated. Designed for 100-yr storm.
Long Ridge Union B with room-and-pillar mining (Union 1979a, 1979b)	8,870	8,062	57 MCY (328 acres)	• WATER BATH QUENCH Cooled to 180 F and moisture content of 29% with stripped sour water.	SIDE-HILL FILL Spent shale will be compacted in 6-8 in. layers of alternating density. Pile will be underlain by 10-ft zone, compacted to 99 pcf at 20.5% moisture; at the end of each year, another 5-ft layer compacted to 99 pcf will be prepared. The intervening material will be compacted to 94 pcf at 22% moisture. The top will consist of a 10-ft zone of permeable and dry material to provide moisture storage and drainage, underlain by a 10-ft layer at 99 pcf.	Runoff will be reused and/or evaporated. Drainage ditches and ponds will be lined with a 3-ft layer of clayey material. Designed for 100-yr, 30-min storm.

[a] Includes other solid wastes that will be codisposed with the spent shale.

[b] Units are: MT = million tons; MCY = million cubic yards; BPD = barrels per day; TPD = tons per day; pcf = pounds per cubic foot.

that four types of final disposal have been proposed: cross-valley fill, surface pile, side-hill fill, and slurry backfill of an underground mine. The most commonly proposed method is the cross-valley fill because of its environmental and cost advantages over other methods.

Surface Disposal

This section will overview the technical aspects of spent shale disposal in various surface configurations, including the cross-valley fill, the side-hill fill, and the surface pile. The important steps or operations in surface spent shale disposal are: (1) spent shale preparation, (2) pile design and development, (3) drainage, and (4) revegetation. Each of these operations should be appropriately considered and simulated in laboratory and modeling studies. Each is briefly reviewed below.

Shale Preparation

Spent shale preparation procedures are dictated by the temperature at which the shale leaves the retort, the final temperature required for safe placement, the moisture content required to achieve the desired field dry density, and by dust control requirements. Generally, safe spreading temperatures have been estimated to be about 160 F (C-b Shale Oil Project, 1976). Field moisture content is set at the maximum dry density, usually between 14% and 25% for spent shales. Additional water may be required for dust control and to replace that lost by evaporation, the quantity generally dependent on the particle size of the spent shale and the placement and compaction methods.

Spent shale exits most retorts at elevated temperatures and must be cooled to a temperature (about 200 F) that will permit safe and reliable transport and disposal. Since it is also usually placed wet to facilitate compaction, water is used for cooling. This may be done by rotary-drum water cooling or by water immersion quenching. The rotary-drum cooling method has been proposed for the TOSCO II retort (C-b Shale Oil Project, 1976; Rio Blanco 1976, 1981; White River Shale Project, 1981). Hot spent shale is introduced into rotary moisturizing-drum coolers where its temperature is reduced by tumbling and by water sprays. Water immersion quenching has been proposed for Superior and Union B retorts which are designed with the bath attached to the retort to achieve a positive seal. In this method, the shale drops from the bottom of the retort into the water quench where it is totally immersed in water. Any steam produced by these systems is condensed in the wet-scrubbing system and recycled. Dust is removed by high efficiency bag houses or scrubbers. A variety of highly contaminated waste streams have been proposed for spent shale cooling including scrubber foam, stripped foul water, plant-area runoff, and mine water (Rio Blanco 1976, 1981; Union 1979a). Some recent work (Stanley et al., 1981; Fox, 1982b; Jackson and Jackson, 1982) has shown that spent shale removes significant quantities of organics and inorganics from retort waters and gas condensates. This sorbed material may be released on disposal by leaching, or it may be volatilized through photodecomposition or alkylation reactions, releasing toxic gases. Thus, the effect of moisturizing water quality on environmental impacts of spent shale disposal should be carefully considered in laboratory studies.

Pile Design and Construction

The quantity and composition of leachate will depend on the state of the pile when leaching occurs. Spent shale may be leached during pile construction and on abandonment. The type and magnitude of impacts that may result during each of these two stages may differ markedly and should be separately considered. During pile construction, unvegetated, fresh spent shale may be leached by snowmelt and rainfall. Following pile completion, surfaces will be revegetated and otherwise modified to control erosion. Construction impacts will depend on specific construction procedures and their sequencing while post-abandonment impacts will depend on final pile configuration and revegetation procedures.

Spent shale piles will be constructed and vegetation established throughout the life of the facility, about 20 years for currently proposed developments. When the pile reaches its final size, it will be contoured and rip rap and other erosion control measures installed. These types of measures will help to control leaching and erosion of pile surfaces on abandonment. However, in intervening years, freshly placed spent shale will be exposed to natural weathering. The importance of this natural weathering will depend on the ability of the drainage system to control surface runoff and on the downward migration of water in the pile. For a typical 100,000 BPD facility, about 50 million tons of fresh spent shale will be placed each year. Snow and thunderstorms characteristic of the oil shale region may significantly interfere with spent shale placement and could lead to unanticipated environmental impacts.

In proposed spent shale disposal schemes, drainage facilities will be installed prior to or in concert with pile construction to collect leachates and to route natural runoff around the pile area. Soils may be stripped and stockpiled for use during revegetation. The disposal pile area may be underlain with a liner constructed out of highly compacted raw or spent shale. The pile itself will be constructed in lifts or windrows of 6 to 24 inches. Each individual lift will be compacted to a specified field density using standard compaction equipment. When the pile reaches it final configuration, the surface will be contoured, erosion control measures emplaced, and the top will be revegetated.

Because of distinct differences in spent shale properties, local climate, and local topography, a variety of specific spent shale disposal plans have been advanced. The only two that are presently being pursued (May 1982) are the Colony Project (USDI, 1975) and the Long Ridge Project (Union, 1979). The Colorado Mined Land Reclamation Board has issued permits for both of these projects, and the interested reader is referred to these permits for more information. Since these include the characteristic features of spent shale disposal, each will be briefly reviewed.

Colony has proposed to dispose of about 19 million tons of spent shale each year, together with about one ton of other solids. This material will be placed in a 900-acre area in Davis Gulch in a cross-valley fill. The final spent shale embankment, shown in Figure 4-1, may be visualized as an earthen dam retaining an earthen fill. Spent shale, moisturized to 10%-15% by weight, will be moved by enclosed overland conveyor and transferred to trucks for transportation to the landfill. Topsoil will be removed ahead

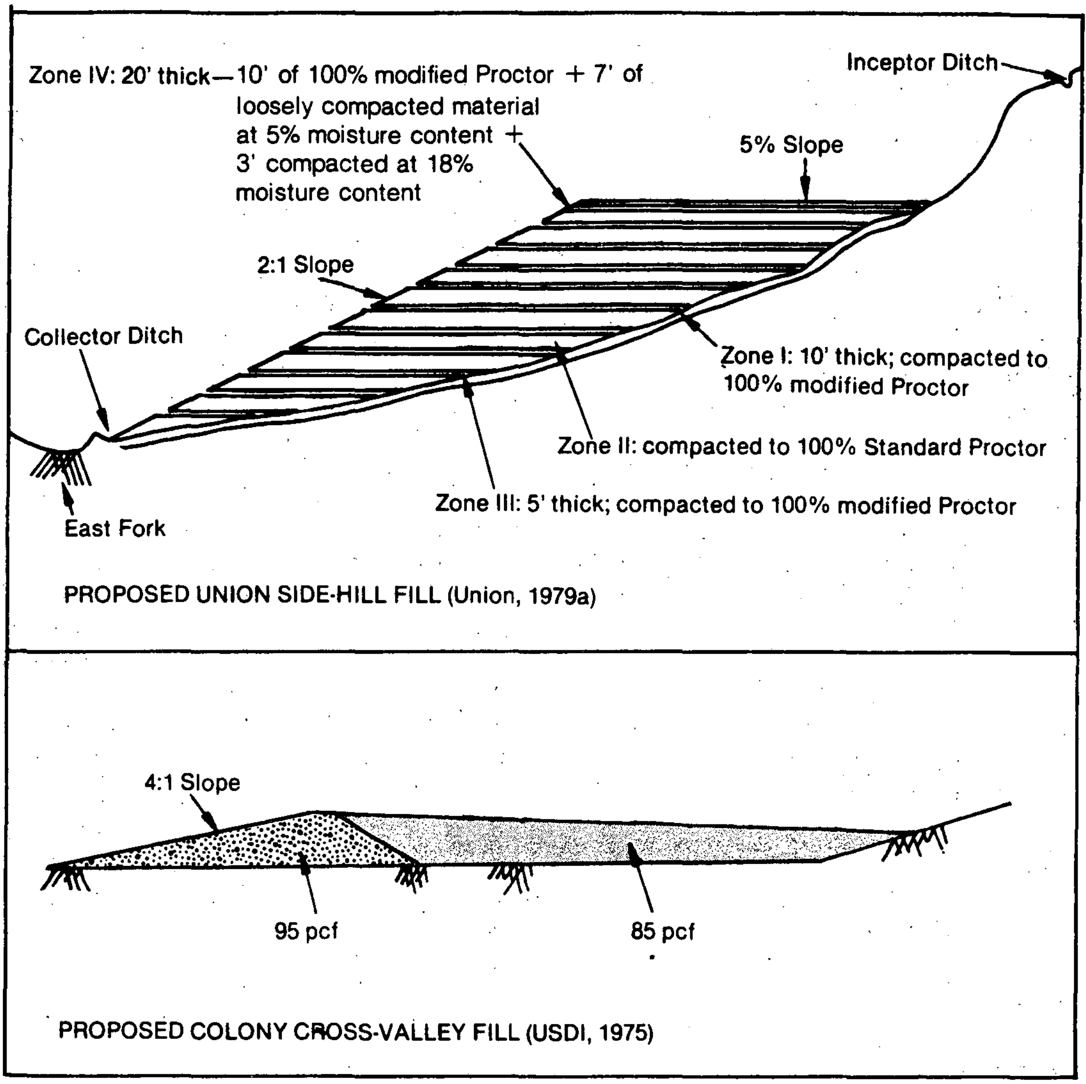

Figure 4-1. Cross-sectional schematics of the proposed Union Long Ridge and Colony spent shale disposal fills.

of filing and stockpiled for use in reclamation. Controlled placement will be accomplished by 150-ton dump trucks spreading discharges 6-18 in. deep across the fill. The bottom 2-ft layer will be supercompacted to provide a virtually impermeable zone. Compaction will be accomplished by a segmented wheel compactor to a density of 95 pcf on the frontal slope and 85 pcf on the interior of the pile. The front slope of the embankment will be constructed on a 4-foot-horizontal to 1-foot-vertical inclination, with horizontal benches at 25-vertical-foot separation. Reclamation will proceed simultaneously with development of the disposal area. Following emplacement of the spent shale, the surface will be scarified to prevent slippage of the topsoil. Top soil will be placed to a depth of about 6 to 12 inches, and the area will be leached by applying 40 inches of water with a sprinkler irrigation system over a 10-day period. Permanent seed mixtures then will be drilled or broadcast, the area will be fertilized, and mulch will be applied. Irrigation for seeding establishment may be required during the first two years following seeding.

Union has proposed a different disposal scheme (Figure 4-1). They will dispose of 57 million cubic yards of spent shale (compacted density) along the East Fork of the Parachute Creek against the north valley wall in a side-hill fill. It has been estimated that the resulting pile will have a maximum height of 750 feet and will be about 13,000 feet long. Spent shale, moisturized to 29% by weight, will be mixed with raw shale fines and transported by conveyor and disposal chute to a truck loading hopper, loaded into 100-ton bottom dump trucks, and laid down in windrows (Cloninger, 1978). These windrows will be spread in 6-8 in. thick lifts (and allowed to cool and dry as necessary) and will be compacted with a smooth-roller vibratory compactor. The pile will be constructed to maintain a 0.5% downward slope of the layers toward the face of the pile. Higher density, relatively impermeable layers will be placed at select locations throughout the pile to control infiltration into the pile during construction. The locations of these impermeable "Zone II" layers are shown in Figure 4-1. The first layer, at the base of the pile, will consist of 10 feet of spent shale compacted to 100% maximum ASTM D-1557 dry density (about 99 pcf at an optimum moisture content of 20.5%; permeability estimated to be about 2.6 ft/yr under a loading of 200 psi). Other similarly compacted, 5-foot-thick layers will be spaced throughout the pile at elevations representing annual completions. The intervening material will be compacted to 100% ASTM D-698 dry density (94 pcf at an optimum moisture content of 22.1%; permeability estimated to be about 8.2 ft/yr under a loading of 200 psi). The top layer will consist of a lower, 10-foot, highly compacted layer overlain by a 10-foot layer of loosely placed spent shale. This loose layer will provide for surface moisture storage and drainage, and it will slope at 5% toward the valley bottom to facilitate drainage. When the pile reaches its final configuration, salts will be leached from the surface, fertilizer will be worked into the loose top layer, and the surface will be revegetated.

Drainage

Drainage systems for spent shale disposal piles are designed to collect and control surface runoff. Downward migration of precipitation is controlled by pile compaction. This strategy is based on the assumption that low permeabilities can be obtained by properly compacting the spent shale, and that this, in combination with the low precipitation and high evapotranspiration in oil shale regions, will prevent significant downward movement of moisture. Although this has been demonstrated in several field and modeling studies (Bloomsburg and Wells, 1978; Metcalf and Eddy, 1975; Holtz, 1976; W. Heley Engineering, 1976) it is still a highly controversial issue which requires further study. The purpose of the present section is to outline the surface drainage control plans proposed for spent shale disposal piles.

Drainage systems for spent shale disposal piles are designed to collect surface leachates and store them for evaporation or in-plant use and/or to intercept runoff originating outside of the pile and route it around or away from the disposal site. These drainage systems typically consist of ditches, flumes, a dam and spillway, and/or ponds which are very conservatively designed for the 100-year storm. The systems proposed for the Colony and Union projects are briefly outlined here.

The Colony system is designed for the probable maximum thunderstorms of 6.5 inches per hour. It consists of a 1200-acre-foot catchment dam to collect and store any contaminated runoff and a system of ditches to collect runoff and direct it to the dam. Drainage flumes will be installed to route runoff from the top of the embankment and surrounding watershed laterally along the edges of the pile. Water stored behind the dam will be used to moisturize spent shale.

The Union system consists of two storage ponds and interceptor and collector ditches designed for the 100-year, 30-minute storm. Runoff tributary to the pile will be diverted and controlled by an interceptor ditch located above the disposal pile (Figure 4-1). This facility will divert and route runoff from the pile around it to natural drainages so that it does not come in contact with the spent shale. Pile runoff will be collected in ditches at the toe of the pile and will be routed to one of two drainage ponds. Pile runoff will flow from the 0.5% surface slope of the pile down the 2:1 face slope and be collected in these ditches. The collection ditches and ponds will be lined with clayey soils to minimize seepage. After pile completion, the 10-foot zone of porous material at the pile surface will provide storage for precipitation, reducing the quantity to be collected. Runoff will be evaporated or used in the plant.

Note that these drainage systems are designed to control runoff during pile construction over the life of the facility. On abandonment, water will no longer be withdrawn from the ponds and dams, and ditches and flumes may silt out, reducing their capacity. These post-abandonment effects should be considered in modeling studies.

Underground Disposal

Spent shale also may be disposed of by backfilling surface or underground mines (combined with surface disposal of the 15% to 25% which cannot be accommodated underground). This method of disposal may lead to groundwater contamination if the mine is located in a water-bearing zone (Figure 1-1). During site operation, the mine would be dewatered. However, on abandonment, groundwaters could reinvade the mine, solubilizing organic and inorganic materials from the stowed spent shale and transporting them in local aquifers.

This disposal method has not been seriously proposed for any conventional oil shale projects (which use underground mines) due to its high costs compared to surface disposal. However, it has been investigated, and some information is available in the public domain (Earnest et al., 1978). It is important to note, however, that if open-pit mining is used, as has been proposed (Lewis, 1980) and widely discussed, it may be necessary to backfill the pits with spent shale. This could lead to environmental problems similar to those identified for in situ retorting and discussed in Chapter 5. The more soluble nature of surface spent shales, compared to in situ ones, could lead to more serious environmental impacts. (This issue has not been addressed in any public or private research known to the author and should receive a high research priority.)

The only proposed commercial oil shale development which is considering backfilling the mine with spent shale and other solids is Superior Oil Company's Multimineral Process (Meredith and Petticrew, 1981; USDI, 1979; Farris and Mains, 1978). This processing method involves the simultaneous recovery of raw nahcolite, shale oil, alumina, and soda ash. In this process, which uses oil shale and associated saline minerals from the northern part of the Piceance Creek Basin, nahcolite first is separated by crushing the raw shale and separating the finer particles which are predominantly nahcolite. Shale oil is extracted from the nahcolite-free rock by retorting it in the Superior indirectly heated retort described in Table 2-1. Alumina and soda ash then are extracted by leaching the retorted shale, followed by selective precipitation. The residuals from these processes -- the leached spent shale, various sludges, collected dust, and retort water -- would be backfilled into the mine which would accommodate 100% of these materials rather than the 75% to 85% typical for other spent shale backfill operations (Meredith and Petticrew, 1981; USDI, 1979). The details of this operation for a proposed experimental facility are described in USDI (1979). The system includes drainage facilities along the panel floors to collect percolate waters drained from the slurry.

The potential environmental impacts of this disposal operation have not been evaluated, and they even were overlooked in the U.S. Department of Interior's Enviromental Impact Statement on the proposed land exchange (USDI, 1979). The impacts of such a disposal operation potentially could be quite severe if the underground mine is not isolated from local groundwaters. During the operational phase of such a project, the site would be dewatered and drainage from the disposed slurry would be collected and recycled. However, on site abandonment, groundwater may reinvade the site, solubilizing organic and inorganic material from the codisposed solids and process waters. Presently, there are inadequate data on the geology and hydrology of the mine zone and on the leaching characteristics of the codisposed materials to evaluate potential impacts, and considerable work is required in this area.

SURFACE SPENT SHALE MINERALOGY

The leachability of surface spent shales depends on the mineral phases that form during retorting and on subsequent reactions that occur during spent shale disposal. Each of these are separately discussed.

Mineral Phases that Form During Retorting

The leaching of inorganic materials from surface spent shales is influenced primarily by the mineralogy of the raw shale and by the effect of specific retorting processes on that mineralogy. Retorting parameters such as maximum temperature, time at temperature, retorting atmosphere, and particle size determine the final characteristics of the spent shale (Table 2-1). The factors that influence the leaching of organics are less well understood, but are believed to include gaseous environment and char combustion (Amy, 1978).

The purpose of this section is to overview the mineralogy of surface spent shales. The organic composition of spent shale will be discussed in the leaching section. Very little information has been published on the mineralogy of spent shales from specific surface processes. Some investigators have qualitatively identified the major mineral phases present in Paraho (Wildung et al, 1980; Townsend and Peterson, 1979; Williamson et al., 1980); TOSCO II (Williamson et al, 1980; Melchior, 1980; Carpenter, 1978); and Lurgi (Mehta and Persoff, 1980) spent shales. Several mechanistic investigations using small laboratory retorts have been conducted that span the range of conditions found in surface processes (Park et al, 1979; Heistand et al., 1978; Burnham et al, 1980; Campbell and Burnham, 1978; Farris, 1979). These mechanistic studies will be briefly overviewed here to provide a framework for interpreting mineralogy and leaching data. Available information on specific spent shales then will be reviewed within this framework.

Several important process parameters for some surface retorts are summarized in Table 2-1. These parameters will affect the mineralogy and leaching characteristics of the resulting spent shale. These processes can be conveniently divided into two classes, based on processing conditions -- those in which char combustion occurs and those in which it does not. Pyrolysis occurs in all of these processes in the rather narrow range of 480 to 540 C in a reducing environment. This pyrolysis step is followed, in most processes, by char combustion to supply process heat. Only Union B and TOSCO II do not combust char. This combustion may either occur within the pyrolysis vessel (Paraho, Superior) or in a separate combustion vessel (Lurgi, Chevron STB), and it occurs at higher temperatures than pyrolysis, usually between 650 and 800 C (see Figure 2-1). The specifics of how char combustion is carried out (temperature, time at temperature, gaseous environment) will largely determine the mineralogy of the spent shale.

The following sections will discuss the major solid-phase reactions which occur during pyrolysis and char combustion in surface retorts. The reaction chemistry of carbonate minerals, silicate minerals, and sulfur minerals will be reviewed and related to leaching behavior. Mineralogy of specific spent shales from commercial processes will be presented and related to reaction chemistry derived from small laboratory reactors.

Carbonate Reactions

The principal mineral phases in raw shale are the carbonates, dolomite and calcite/ankerite, which together constitute about 50% of the mineral matrix (Table 3-3). (Ankerite is a dolomite in which Fe^{+2} has been isomorphously substituted for Mg^{+2}.) Nahcolite and dawsonite are also major minerals in the north-central part of the Piceance Creek Basin (see literature review by Farris and Leland, 1978). These minerals may undergo decomposition and solid-phase reactions under the conditions encountered in surface retorts. These reactions are important in leachate chemistry because they may produce relatively soluble oxides (CaO, MgO) which release high concentrations of Ca, Mg, and OH in aqueous solution.

The reactions of these minerals in oil shale retorts have been extensively studied since they are endothermic and require large amounts of process heat. The principal carbonate decomposition reactions are summarized in Table 4-2. Generally, nahcolite and dawsonite will decompose in all surface processes during the pyrolysis step. Calcite, dolomite, and ankerite decompose only at the higher temperatures encountered during char combustion. This is illustrated by Figure 4-2 which summarizes the mineralogical changes that occur in 100% N_2 and 100% CO_2 atmosphere as a function of maximum temperature. Most surface retorts are designed to operate below the calcite decomposition temperature.

TABLE 4-2

Principal Carbonate Minerals[a] Naturally Occurring in Colorado Oil Shale. The Decomposition Reactions Shown Are Those That Would Be Expected for Pure Phase Materials and the Temperature Range Is for a Heating Rate of 0.033 K/s (2 C/min). Note That Some of the Reactions As Written Are Not Stoichiometric.

Mineral	Reaction	Temperature Range (^oC)	Enthalpy of Reaction[b] kcal/mole
Nahcolite	$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$	$\sim$100-120	26.6
Dawsonite	$2NaAl(OH)_2CO_3 \longrightarrow Na_2CO_3 + Al_2O_3 + 2H_2O + CO_2$	$\sim$350-400	
Dolomite	$CaMg(CO_3)_2 \xrightarrow{P_{CO_2} = 0} MgO + CaO + 2CO_2$	$\sim$600-750	72
	$\xrightarrow{P_{CO_2} \neq 0} MgO + CaCO_3 + CO_2$	$\sim$600-750	31
Calcite	$CaCO_3 \longrightarrow CaO + CO_2$	$\sim$600-900	41
Ankerite	$Ca(Mg_{1-x}Fe_x)(CO_3)_2 \xrightarrow{P_{CO_2} = 0} Fe_2O_3$[c] $+ MgO + CaO + 2CO_2$	$\sim$600-750	$\sim$70
	$\xrightarrow{P_{CO_2} \neq 0} Fe_2O_3 + CaCO_3 + MgO + CO_2$	$\sim$600-750	$\sim$30

[a] Small quantities of other carbonate minerals have been reported in oil shale (e.g., siderite and ferroan); in this study, however, only the major mineral carbonate species are considered.

[b] Enthalpies are per mole of original carbonate (i.e., reactant).

[c] Only the ferric product has been reported from x-ray analysis.

Source: Campbell and Burnham, 1978

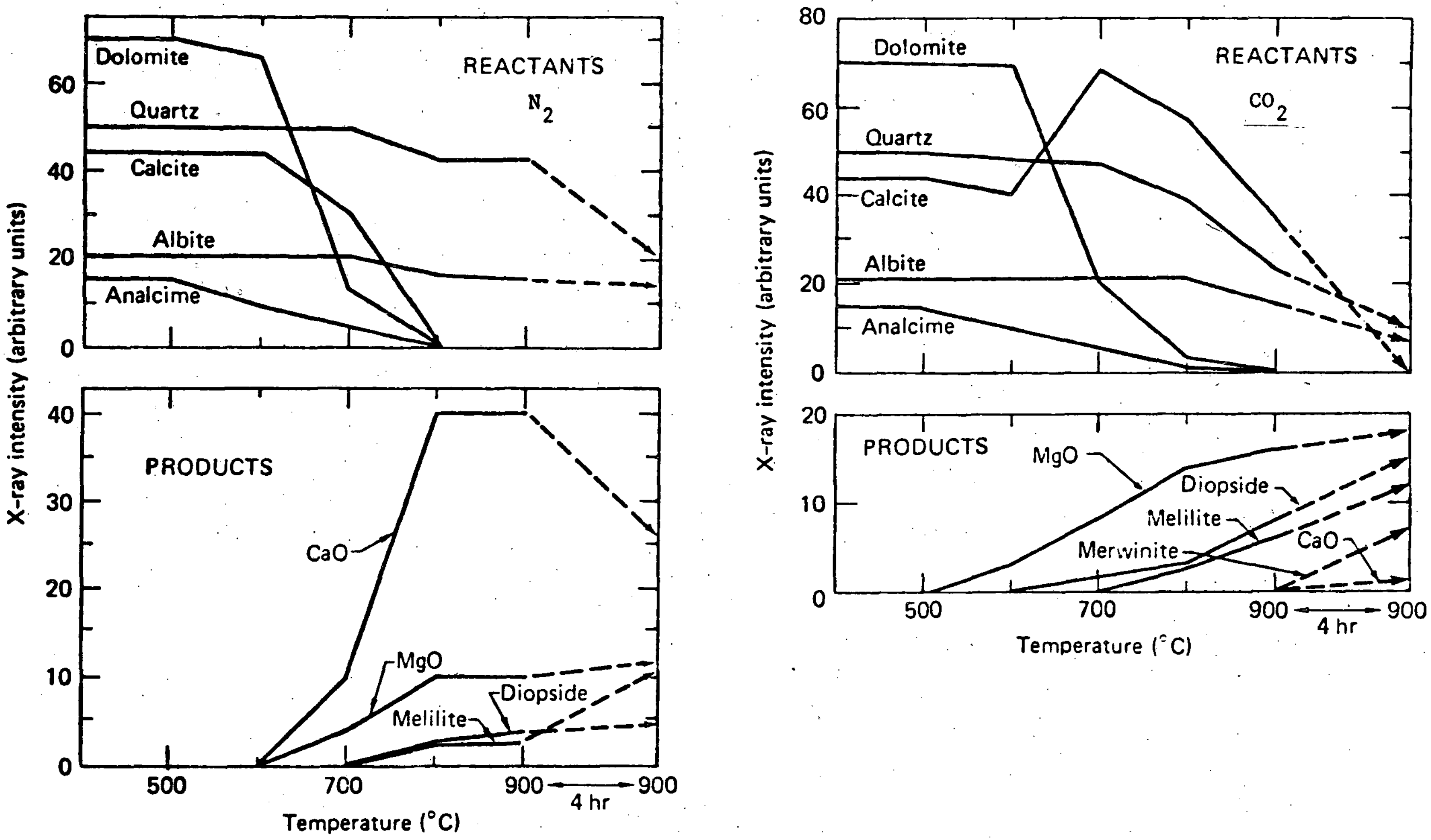

Figure 4-2. X-ray diffraction intensities versus temperature for laboratory retorting experiments in 100% CO_2 and 100% N_2. Anvil Points raw shale was heated to temperature at 4 C/min and immediately cooled. (Burnham et al., 1980).

Carbonate decomposition occurs only if the CO_2 overpressure satisfies the relationship (Burnham et al., 1980):

$$P_{CO_2} \leq K_{eq}.$$

For dolomite, K_{eq} is greater than 10 atm for temperatures greater than 600 C so dolomite decomposition is not inhibited by CO_2 overpresssure in oil shale retorts. However, if the CO_2 pressure is nonzero, calcite rather than CaO will be formed from dolomite decomposition, or

$$\begin{tikzcd} & MgO + CaO + 2CO_2 \\ CaMg(CO_3)_2 \arrow[ur, "P_{CO_2} = 0"] \arrow[dr, "P_{CO_2} \neq 0"] & \\ & MgO + CaCO_3 + CO_2 \end{tikzcd}$$

The calcite formed from this reaction, plus the calcite originally present in the oil shale decompose at some higher temperature, depending on the CO_2 overpressure. For calcite, K_{eq} varies from approximately 0.01 atm at 600 C to about 1 atm at 900 C (Burnham et al., 1980). Thus, for very small CO_2 partial pressures, calcite and dolomite will decompose at approximately the same temperature. For CO_2 pressures near 1 atm, the calcite decomposition temperature is about 200 C greater than for dolomite.

The effect of time at temperature on carbonate decomposition is shown in Figure 4-3 which summarizes mineralogical changes that occur as a function of time when pellets of Logan Wash raw shale are heated to 600 and 760 C in a 1% N_2-O_2 and 100% CO_2 atmosphere. Relatively long residence times (greater than about 1 hour) in air (Heistand et al., 1980), nitrogen (Burnham et al., 1980), or 1% N_2-O_2 (Park et al., 1979) atmospheres and temperatures greater than 600 C result in the formation of periclase (MgO) and lime (CaO). These conditions are similar to those found in the char combustion section of the Paraho direct retort (Figure 2-1).

On the other hand, little carbonate decomposition occurs for very short residence times, from seconds to minutes. These conditions are similar to those found in fluidized-bed combustion processes such as in the Lurgi lift pipe and the Chevron staged turbulent bed. The carbonate (and silicate) mineralogy of spent shales from these processes should resemble raw shale mineralogy. However, other mineral phases including analcime and the clays, will be altered.

Silication Reactions

Oil shale contains not only carbonates, but also significant quantities of quartz and other silicates (Table 3-3). The carbonates and metal oxides formed by carbonate decomposition may react with these silicates to produce relatively insoluble calcium-magnesium silicates.

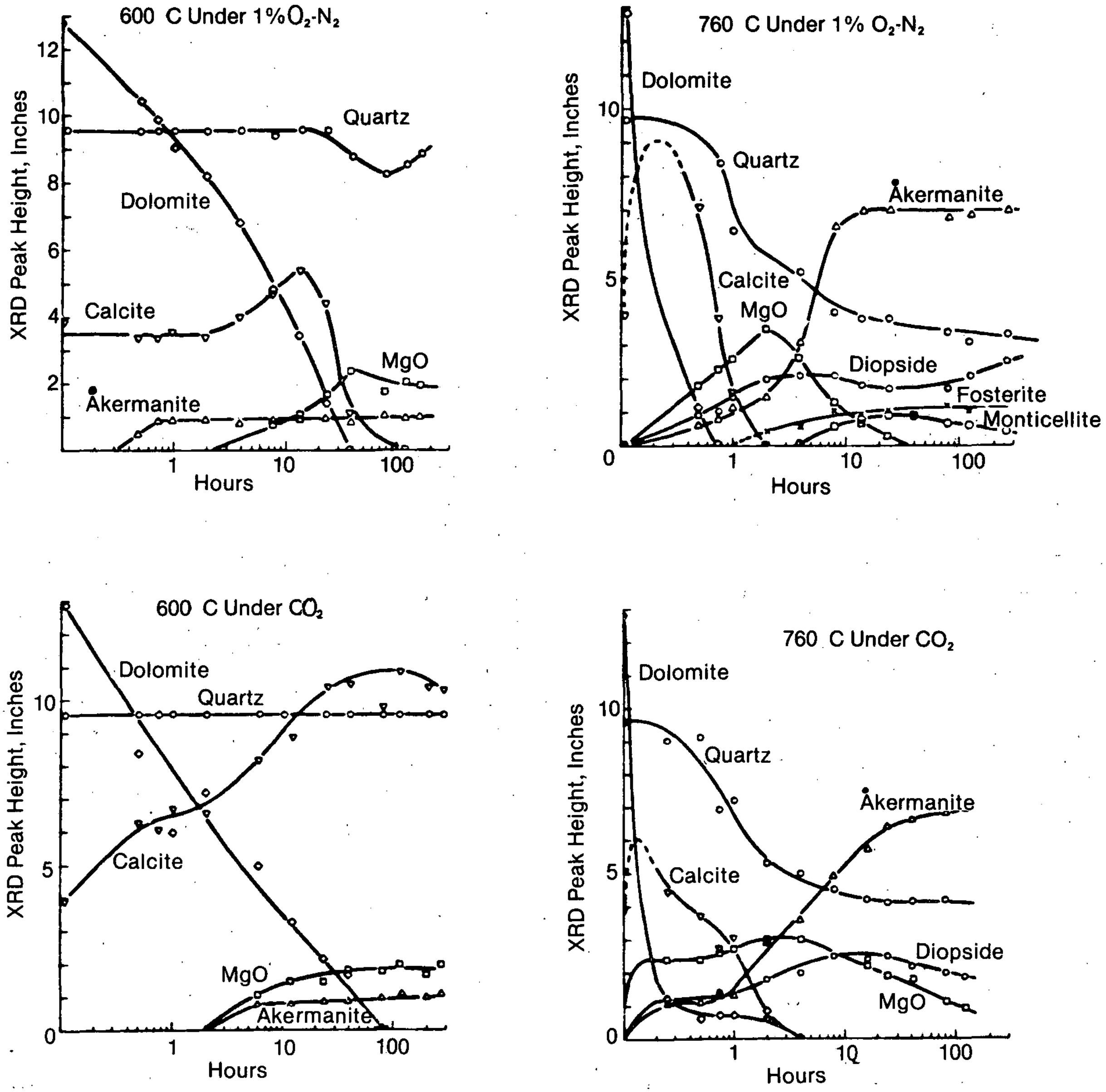

Figure 4-3. X-ray diffraction peak heights in inches versus time for isothermal retorting experiments in which pellets of Logan Wash raw shale were heated to 600 C and 760 C under 1% O_2-N_2 and 100% CO_2 atmospheres (Park et al., 1979).

These types of reactions are relatively more important for in situ processes where the requisite high temperatures and long residence times are achieved. However, the work of Park et al. (1979) and of Burnham et al. (1980) suggest that some of these silicates may form during char combustion in some surface retorts. Some of the possible reaction products were shown in Figure 4-2 as a function of temperature in 100% N_2 and 100% CO_2 atmospheres. Others are shown in Figure 4-3 as a function of retorting time at 600 C and 760 C in a 1% O_2-N_2 atmosphere and a 100% CO_2 atmosphere. These results suggest that akermanite, diopside, forsterite, and melilite may form under conditions found in surface retorts.

Sulfur Reactions

The reactions that sulfur compounds in raw oil shale undergo during retorting are also important in interpreting leaching behavior of spent shales. Several studies have shown that about 63% to 77% of the sulfur in oil shale is present as pyrite, that 1% to 3% is present as sulfate, and that the balance or 22% to 30% is organically bound (Stanfield et al., 1951; Smith et al., 1964; Burnham, 1982). Mineralogical studies, recently reviewed by Fitzpatrick (1982), reveal that reduced sulfur species present in the Green River Formation in Colorado include native sulfur, pyrite, pyrrhotite, and wurtzite (ZnS), and that the latter three (FeS_2, FeS, and ZnS) are ubiquitous, though present in small concentrations. Mercasite (FeS_2) also is locally abundant, especially in Utah (Burnham, 1982). Sulfate minerals are believed to be secondary alterations of pyrite and other sulfides and include gypsum ($CaSO_4 \cdot 2H_2O$); szomolnokite ($FeSO_4 \cdot H_2O$); barite ($BaSO_4$); starkeyite ($MgSO_4 \cdot 4H_2O$); and bloedite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$) (Brobst and Tucker, 1973; Milton and Eugster, 1959; Milton, 1977). Relatively little is known of the fate of the organic and sulfate forms during retorting. However, the decomposition and subsequent reactions of pyritic sulfur have been investigated (Taylor et al., 1982; Burnham and Taylor, 1982).

Burnham et al. (1981) have proposed that the dominant sulfur reaction during pyrolysis is the reduction of pyrite by hydrogen to form pyrrhotite and hydrogen sulfide:

$$FeS_2 + 2H \longrightarrow FeS + H_2S$$

The pyrrhotite formed in this reaction is not easily reduced to Fe at temperatures below 900 C and, thus, pyrrhotite should be the principal sulfur mineral in spent shales from pyrolysis of oil shale (i.e., Union B and TOSCO II).

The pyrrhotite in pyrolyzed spent shale can be oxidized to iron oxide and sulfur dioxide during char combustion (Taylor et al., 1982):

$$FeS + \frac{7}{4} O_2 \longrightarrow \frac{1}{2} Fe_2O_3 + SO_2$$

The sulfur dioxide produced by this reaction reacts with carbonates to form sulfates:

$$2FeS + CaMg(CO_3)_2 + \frac{9}{2} O_2 \longrightarrow Fe_2O_3 + CaSO_4 + MgSO_4 + 2CO_2$$

Taylor et al. (1982) have shown that equal amounts of calcium and magnesium sulfates form below 600 C and only calcium sulfate forms above 700 C.

In the Lurgi and Chevron processes, additional reactions may occur which result in the formation of sulfides. In these processes, hot oxidized spent shale is the heat transfer medium and is mixed with raw shale in the lift pipe (Figures 2-5, 2-6). It has been hypothesized that the oxidized sulfur species ($CaSO_4$, $MgSO_4$), oxides (CaO, MgO), and carbonates ($CaCO_3$, $CaMg(CO_3)_2$) may be reduced to calcium sulfide (CaS) (Burnham and Taylor, 1982). Recent work indicates that the thermodynamics are unfavorable for forming magnesium sulfide (MgS) (Burnham, 1982). The specific reactions presently are uncertain. Therefore, the portion of the spent shale in these processes which is used for heat transfer may have a different composition than the portion which is oxidized and directly disposed. This points to the great importance of carefully specifying the origin of spent shale samples.

This proposed sulfur reaction chemistry has some important implications for leachate chemistry due to the differences in solubility of sulfides (relatively insoluble), sulfates (relatively soluble), oxides, and carbonates. Some pertinent solubility data for the important species that participate in sulfur reactions are summarized in Table 4-3. The effect of these reactions on the leachability of sulfur from spent shale is summarized in Figure 4-4. In unoxidized samples (TOSCO II, Union B), the principal sulfur species is pyrrhotite, which is sparingly soluble (0.0006 g/100 g) and pyrite which is insoluble. Less than 20% of the available sulfur is leached from unoxidized samples. In oxidized samples (Superior, Paraho direct, and oxidized Chevron and Lurgi), the principal sulfur species would be $CaSO_4$ and/or $MgSO_4$, which are soluble. The quantity of sulfur leached increases as a function of oxidation temperature. Since the temperature during char combustion ranges from 600 to less than 700 C, nearly 100% of the available sulfur may be solubilized during leaching. Finally, for oxidized samples that are reduced during heat transfer in a lift pipe (Chevron, Lurgi), CaS or other sulfides may be the principal sulfur species. These are relatively insoluble compared to the sulfates.

Mineral Phases in Spent Shales From Commercial Processes

This theoretical framework will now be compared with actual measurements on spent shales from specific processes. The reader is cautioned that surface retorting technology is under development and that as demonstration plants are built and operated, changes in processing variables may be made to improve oil yields and energy balances. These changes may alter the mineralogy of the spent shale. Thus, too much emphasis should not be placed on detailed characterizations of specific spent shales. Rather, the broader approach previously presented is more useful.

TOSCO II

Carpenter (1978) and Williamson et al. (1980) have studied the major mineralogy of TOSCO II spent shale. Carpenter (1978) used powder x-ray diffraction (XRD) techniques to identify quartz, dolomite, calcite, rutile (TiO_2), pyrite, albite, and Na-feldspar as the major minerals. He concluded that little degradation of the original mineral components had occurred during retorting.

TABLE 4-3

Solubility Data for Some Important Sulfides, Carbonates and Oxides in Surface Retorts (Dean, 1979).

Compound	Solubility (g/100g)
$CaCO_3$	0.0013
CaO	0.13
$CaSO_4$	0.2
CaS	0.02
$MgCO_3$	0.01
MgO	i[c]
$MgSO_4$	125[a]
MgS	--[b]
$FeSO_4 \cdot 5H_2O$	42
FeS_2	i[c]
FeS	0.0006

[a] Windholz et al., 1976

[b] No data found

[c] Insoluble

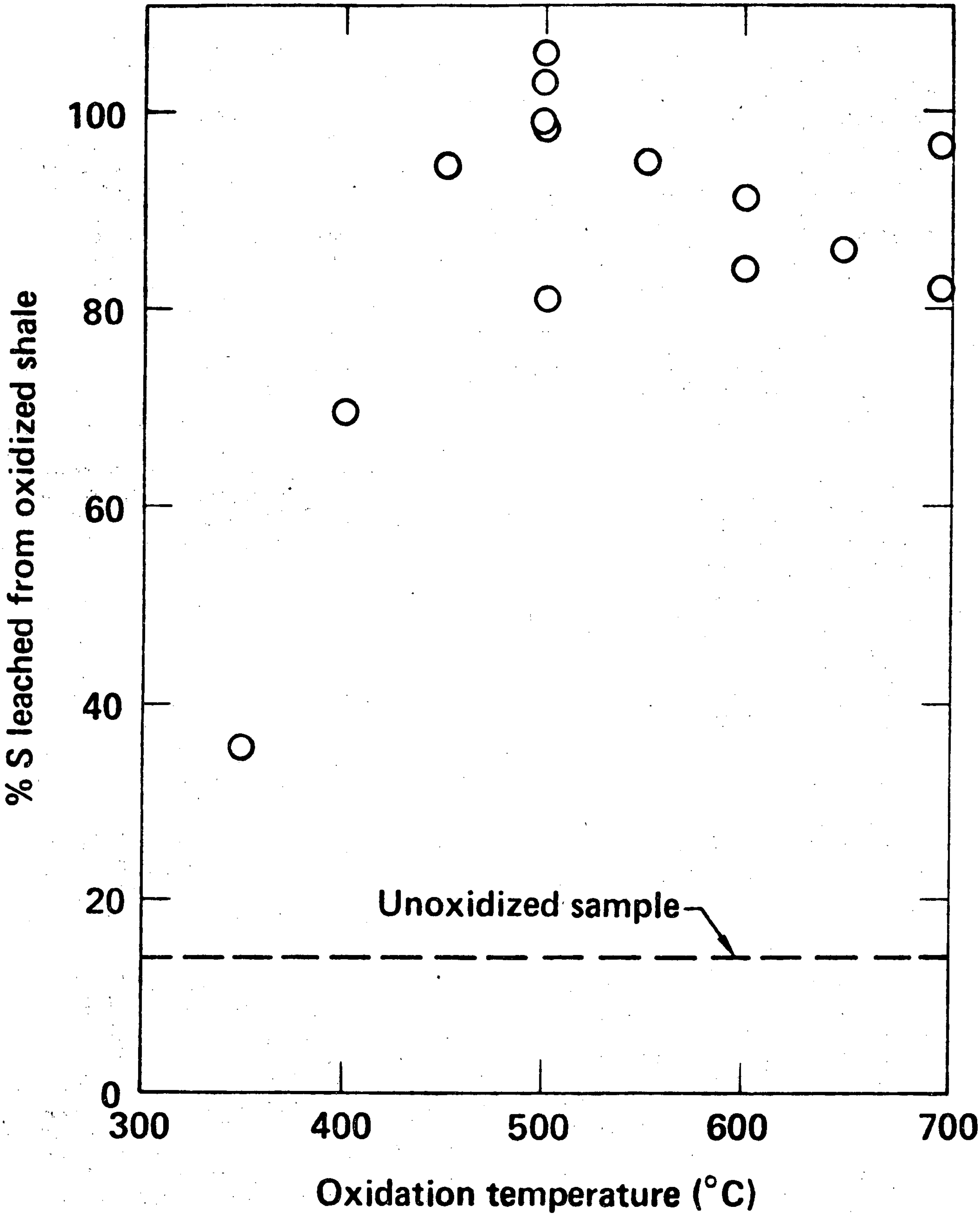

Figure 4-4. The fraction of sulfur leached from oxidized and unoxidized spent shale as a function of temperature. Length of oxidation was 30 min. (Taylor et al., 1982).

Williamson et al. (1980) and Melchior (1980) used Mossbauer spectroscopy to identify the iron minerals present in raw and spent shale from the TOSCO and Paraho processes. Their data are summarized in Table 4-4. This work demonstrated that ankerite $(Mg,Fe)Ca(CO_3)_2$ is not decomposed in the TOSCO II retort while some of the pyrite (FeS_2) is converted to pyrrhotite (FeS). These results are largely consistent with the laboratory mechanistic studies summarized above which predict that the major minerals in raw shale are stable at temperatures below 600 C and that pyrite is reduced to pyrrhotite during pyrolysis. Carpenter's failure to detect pyrrhotite in his sample is probably because it was below the detection limit of his XRD technique.

TABLE 4-4

Iron Minerals in Raw and Spent Shales From the Paraho and TOSCO Processes (Williamson et al., 1980).

	Percent Iron (%)				
Sample	Pyrite (FeS_2)	Ankerite [$Ca(Mg,Fe)(CO_3)_2$]	Hematite (Fe_2O_3)	Magnetite (Fe_3O_4)	Pyrrhotite (FeS)
TOSCO II raw	40	60			
TOSCO II spent	24	61			15
Paraho raw	20	75			5
Paraho spent	19	37	33[a]	6	5

[a] Combination of hematite and magnetite.

Paraho Direct

The major mineral phases in Paraho direct spent shale have been studied by Townsend and Peterson (1979), by Wildung et al. (1980), and by Williamson et al. (1980). X-ray diffraction analyses revealed that Paraho spent shale is similar to that of the raw shale and that the major minerals are quartz, feldspar, dolomite, clay-mica, and usually, analcime and calcite.

Wildung et al. (1980) demonstrated that dolomite undergoes partial decomposition to calcite and periclase. Similarly, Townsend and Peterson (1979) observed that calcite is usually higher than dolomite in the spent shale while the reverse is true for the raw shale. They also tentatively identified periclase and calcium sulfate. Wildung et al. (1980) also reported that nahcolite decomposes to Na_2O_3; that analcime is dehydrated and partially decomposed; and that illitic phyllosilicates collapse in Paraho spent shale. These results are all consistent with laboratory studies which predict the decomposition of carbonate minerals above 600 C and the formation of lime, periclase, and calcite (Heistand et al., 1980). Although lime was not detected in these studies, this may be due to the overlap of quartz, feldspar and other peaks with that of lime.

In other work, Williamson et al. (1980) found that ankerite had partially decomposed to yield hematite (Fe_2O_3) and magentite (Fe_3O_4) and that pyrite and pyrrhotite were unchanged by retorting (Table 4-4). This latter observation is inconsistent with Wildung's work, who noted the partial reduction of pyrite to pyrrhotite, and with expected sulfur chemistry (Taylor et al., 1982; Burnham and Taylor, 1982). This inconsistency in the work of Williamson et al. (1980) is probably due to an analytical problem.

Lurgi

Mehta and Persoff (1980) studied a sample of Lurgi spent shale from the electrostatic precipitator (Figure 2-5) that had been retorted at 650 C and combusted at 700 C. X-ray diffraction revealed that the major minerals were dolomite, quartz, calcite, and feldspar. No periclase or lime was detected, and the loss on ignition was 20%. These results suggest that little or no decomposition of the carbonates occurred. This is consistent with the short residence time in the Lurgi lift pipe. Although the combustion temperature is high enough (700 C) to decompose dolomite, the length of time that the shale is exposed to this high temperature is too short to significantly decompose it. These results are consistent with those predicted from laboratory mechanistic studies.

Mineral Phases That Form During Disposal

Other mineralogical reactions may occur in the field when the spent shale has been moistened, compacted, and cured. Several investigators have noted the natural cementing tendencies of spent shales (Culbertson et al., 1970; Holtz, 1976; Townsend and Peterson, 1979; Farris, 1979). These investigators variously noted that compressive strengths increase or that permeabilities decrease with increasing curing time. Farris (1979) studied this behavior in a laboratory retort that was operated for a range of gas compositions, temperatures, and residence times selected to span those found in surface retorts. He observed that retorting temperature, residence time, and mode of heating had a significant effect on cementation strength. He found that optimum conditions for natural cementation were 822 C for 2.0 hours for direct-mode processes (270 psi) and 832 C for 2.9 hours for indirect-mode processes (325 psi). Optical microscopy, scanning electron microscopy, and x-ray diffraction analyses revealed that the cementation mechanism was the growth and interlocking of secondary crystals of calcium aluminum sulfate at the points of contact between the spent shale fragments. These and other mineralogical reactions may occur in the field which will alter the leaching behavior of spent shales.

SURFACE SPENT SHALE LEACHATES

Surface retorting of oil shale will produce large quantities of spent shale which will be disposed of in cross-valley fills, side-hill fills, surface piles, or mine backfills (Table 4-1). Disposal operations will be continuous, over the life of a facility, with placement, compaction, and revegetation occurring simultaneously in different sections of the disposal area. Effluents will be generated by the interaction of the natural environment with the disposal sites (Figure 1-1). Spent shale disposed of by surface techniques will be exposed to rainfall and snowmelt which may run off of the pile surface or percolate through it, reaching nearby surface and ground waters. Spent shale used to backfill open pits or underground mines may be leached by groundwater or rainfall infiltration. Slurry water used to control dust, to cool spent shale, and to facilitate compaction, may drain from the disposal sites. This drainage may be more prevalent in surface configurations due to elevated pressures at the base of piles.

The nature and magnitude of the resulting environmental impacts will depend on the type of disposal method, reclamation procedures, and drainage system design. All presently proposed pile designs assume that surface runoff can be intercepted and routed around the site, or collected for evaporation or in-plant use. These same designs assume that percolation can be controlled by proper pile compaction. Conventional pile liners and underground drainage systems are not included in most designs.

Early research on surface spent shale runoff (Margheim, 1975; Ward et al., 1971; Ward and Reinecke, 1972; Metcalf and Eddy, 1975) demonstrated that most dissolved constituents reach low levels (1-10 ppm) following 5 to 10 minutes of runoff and that even the peak concentrations are modest compared to percolation quality. Only suspended sediment is high and remains so throughout a runoff event (10-50 g/L). Since sediment can be easily controlled by conventional drainage systems and erosion control measures, which industry incorporated into their disposal plans, researchers turned their attention to percolation, where the focus of the research, and the controversy, has remained for the past decade. However, this does not mean that surface runoff is an unimportant problem. Subsequent work demonstrated that runoff from non-topsoiled spent shale piles has high sodium adsorption ratios (SAR) and dissolved salts (Harbert and Berg, 1978; Kilkelly et al., 1981; Harbert et al., 1979). Runoff water quality may be important for spent shale piles that are not covered with a layer of topsoil or for those in which the topsoil has eroded.

The quantity and composition of these leachates, especially percolation, is of great interest due to their potential adverse affects on water resources of the oil shale region. This interest is reflected by the large number of studies that has been conducted on them over the past decade (Appendix Table A-2). However, in spite of this considerable quantity of work, much controversy and uncertainty remains. We still do not understand moisture movement through spent shale piles. There is great variability in reported laboratory leachate concentrations for the same process, and the composition of leachates from a commercial disposal pile is uncertain. These uncertainties are due to several factors, including changes in surface retorting technology; lack of adequate quantities of fresh, representative spent shale; limitations of simple laboratory leaching procedures; a failure to relate leaching characteristics to spent shale mineralogy; and an inadequate understanding of the vagaries of the natural environment and their interactions with our samples. These types of issues must be considered when evaluating and reviewing the considerable volume of surface spent shale leaching information, and some of the more important issues are overviewed here.

Industry has been developing retorting technologies for several decades. The familiar process configurations that come to mind today are different in important ways from those that were being tested ten years ago or even two or three years ago. And more changes will occur as the industry matures. Transformations have occurred in important variables such as retorting temperature and gas handling, which control spent shale mineralogy and leachability. Other changes have involved shifts in particle size ranges or raw shale sources. Some companies have renamed their processes as a result of major alterations (Union A, B, and SGR) while many other changes are subtle and less well known. Laboratory scientists have studied spent shales generated throughout a decade or more of changes without noting processing conditions. The result is that spent shales with widely varying leaching characteristics are now uniformly labeled "TOSCO II", "Union", etc. This has contributed to the variability in reported leachate compositions. Runnells and Esmaili (1981), for example, found significant differences in leachate composition among two samples of "TOSCO II" spent shale in which the same test methods were used.

A related problem is that of sample history, from the time the spent shale is cooled and discharged from the retort until it finds itself in a scientist's beaker. Information on spent shale cooling is rarely, if ever, available. Unfortunately, a variety of cooling methods, including steam, air, and recycle gas, have been investigated in the past decade, and these may strongly affect leachate composition. The use of recycle or other process gases may lead to adsorption of organics on the spent shale while different gaseous atmospheres and temperature profiles during cooling will affect environmentally important mineralogical reactions, altering leachate composition. This is compounded by variable storage conditions. Some samples have been collected directly from indoor pilot plants and immediately studied. Others were discarded in outdoor disposal piles and sampled anywhere from a few months to ten or more years later. Several studies (Schmidt-Collerus, 1975; Schmehl and McCaslin, 1973; Wildung and Zachara, 1981; Garland et al., 1979) have noted significant differences in leachate composition, depending upon sample age and weathering. The majority of the surface spent shale samples that have been studied do not have recorded histories. There is no record of their origin (indoor retort, outside disposal pile), their age on collection and analysis, or storage conditions following sampling.

An equally important and perplexing issue is the simulation of leaching phenomena in the laboratory. The natural environment is exceedingly complex and is difficult to model in simple experiments using beakers and glass columns. The vagaries of climate and the mysteries of microbial action result in a complex natural system. Surface spent shale leaching investigations initially focused on exhaustive chemical characterizations and more recently, on developing a mechanistic understanding of fundamental chemical, physical, and biological processes. A diversity of techniques ranging from Soxhlet extraction to blenders to static batch tests to column studies, and a wide range of experimental conditions (various particle sizes, solid-to-liquid ratios, etc.), have been used to probe leaching phenomena. This work has been complemented by field lysimeter studies. These different methods also have contributed to variability in leachate data.

With these caveats in mind, the available data on surface spent shale leaching will be discussed. Published literature on leaching (percolation and runoff) is summarized in Table A-2.

CHARACTERIZATION OF SURFACE SPENT SHALE LEACHATES

Accurate characterizations of leachates are necessary to assess the impact of spent shale disposal plans on surface and ground water quality and to evaluate and compare various disposal techniques. Unfortunately, the available data are not adequate for these purposes, as discussed previously. However, the data can be used to estimate probable compositions and differences among processes, which will be done in this section.

The review of published studies summarized in Table A-2 reveals two interesting facts. First, the vast majority of the surface spent shale leaching work was done with samples from the Paraho and TOSCO II processes. A few recent studies have used Union B (Union, 1979c; Cleave et al., 1980), a single study has investigated Superior spent shale (Jackson and Jackson, 1982), and there is no published information on the leaching characteristics of Chevron STB or Lurgi spent shales. The second interesting observation is that a single, standardized leaching procedure has not been used to uniformly compare these spent shales. A wide range of leaching procedures and experimental variables has been used, each affecting the composition of the resulting leachate. There is no common thread among these studies, and thus, it is difficult to compare various spent shales or to corroborate the work performed by different investigators. Work is in progress at CSU (Bates, 1981) to develop a reproducible column leaching test that will be used to evaluate all of the commonly available surface spent shales (Lurgi, Chevron, Paraho, and TOSCO II).

In this section, leachates from various processes will be compared, highlighting important process-related differences. Then, the specific relevant data for each process for inorganic and organic composition will be reviewed in greater detail.

Overview

Table 4-5 summarizes the salient characteristics of leachates produced by batch tests of Paraho, TOSCO II, and Union B spent shale. Uniform leaching procedures were not used to generate the data for all three processes. However, data have been selected that are comparable, based on best available information.

This comparison shows that there are some significant differences in the major and minor elemental concentrations in leachates from these three processes. These differences are generally consistent with the mineralogy discussed previously. Distinctions among the direct (Paraho) and indirect (Union B, TOSCO II) and between the two indirect processes, are particualrly notable. The Paraho direct-mode leachate has the highest reported concentrations of Ca, Mg, K, SO_4, Li, and TDS and the highest reported pH. The uniquely high pH and Ca concentration results from the hydrolysis of MgO and dissolution of $CaSO_4$ while the uniquely high Mg concentration likely results from the dissolution of $MgSO_4$ and MgO. Similarly, the high SO_4 concentration is due to the dissolution of $MgSO_4$ and $CaSO_4$ and is consistent with the decomposition of pyrite to pyrrhotite and subsequent formation of sulfates during combustion (Taylor et al., 1982). The elevated K probably originates from the collapse of illitic phyllosilicate (Wildung et al., 1980). The cause of the

TABLE 4-5

Comparison of Leachate Composition From Three Surface Retorting Processes (mg/L) Produced in Batch Tests Using Shale-to-Water Ratios of 0.1 to 0.4 g/mL and Contact Times of 30 Minutes to 17 Days (Cleave et al., 1979; Runnells and Esmaili, 1981; Stollenwerk, 1980; Garland et al., 1979).

	Union B	TOSCO II	Paraho Direct
Major Cations			
Na	110	820	820
Ca	240	2	650
Mg	60	0.4	250
K	7	8	60
Major Anions			
SO_4	880	630	4300
HCO_3	170	20	180
Cl	7	20	30
CO_3	0	--	15
Trace Elements			
B	1	5	1
F	6	80	7
Mo	0.4	3	0.8
Li	0.1	<0.1	6-20
Water Quality Parameters			
TDS	1520	2200	7100
TOC	10	100	2
pH	8	8	10

uniquely high Li concentration, noted by Wildung and coworkers (Wildung et al., 1980-1981), is uncertain. The Paraho leachate also has the lowest organic carbon concentration among those studied. This is hypothesized to be caused by oxidizing conditions in the Paraho retort. Some of the residual carbon on the spent shale and recycle gas are burned to supply process heat.

The relatively lower concentrations of Ca, Mg, K, and SO_4 and the lower pH of the Union B and TOSCO II leachates are a consequence of the reducing atmosphere, the lower temperatures, and the absence of char combustion. Little or none of the dolomite decomposes during pyrolysis (Figures 4-2, 4-3), and sulfide oxidation and subsequent capture of SO_2 to form soluble sulfates do not occur. Thus, the absence of lime probably accounts for the lower pH while the lower Ca concentrations are due to the absence of both CaO and char-combustion $CaSO_4$. Similarly, the low sulfate concentrations in Union B and TOSCO II leachates compared to Paraho direct leachates are due to the absence of char-combustion $CaSO_4$ and $MgSO_4$. The sulfate in the TOSCO II and Union B leachates probably originates from the dissolution of sulfate originally present in the raw shale and from the oxidation of FeS_2 and FeS(?). The lower K concentrations may be due to the failure of illite to decompose under pyrolysis conditions (conjecture). Lower TDS concentrations are due to both the less soluble nature of minerals in the spent shales (oxides and sulfates are largely absent) and to the lower pH which reduces the attack of alkaline leachates on silicates and other minerals. The higher TOC concentrations are probably due to the desorption of organic compounds associated with the unconverted char. The cause for the different behaviors among the trace elements is unknown due to the absence of information on minor mineralogy and the effect of retorting conditions on it.

There are also some interesting differences between the two types of indirect spent shale. A comparison of the Union B and TOSCO II leachates indicates that the concentration of Ca, Mg, SO_4, and HCO_3 are significantly higher in Union B leachates and that Na, B, F, and Mo are significantly lower than in TOSCO II leachates. Although this is probably related to differences in pyrolysis temperature and gas environments, there is inadequate information to specify reaction pathways or to separate differences due to raw shale mineralogy and processing conditions. A few possibilities are advanced here for select constituents. The concentration of F in TOSCO II and other leachates in controlled by the secondary mineral, CaF_2, (Saether, 1980; Stollenwerk, 1980; Peterson et al., 1982). Thus, the notably high F concentration, 60 mg/L, is probably due to the low Ca concentration, 2 mg/L. The uniquely high TOC concentration in TOSCO II leachate is hypothesized to be due to absorption of organics from the pyrolysis gases onto the spent shale. In the Union B process, the pyrolysis gases move countercurrent to the spent shale, minimizing the contact time between gas and shale. Other differences are not understood, and mineralogical investigations would be required to explain them.

Inorganic Composition of Surface Leachates

The purpose of this section is to summarize inorganic characterization information for surface spent shales. The problems of presenting reliable characterizations were already discussed. Thus, the important results for each process will be presented here.

In general, leachates from surface spent shales that have been studied to date are alkaline Na_2SO_4 solutions with high concentrations of Ca, Mg, Cl, K, and/or HCO_3. The trace elements that are elevated usually include F, B, Mo, Li, and/or V. Carbonate and sulfur chemistry of these leachates are important and control/dominate solution chemistry, pH, and redox state.

TOSCO II

The inorganic composition of TOSCO II leachates has been studied for a decade in laboratory column and batch studies (Stollenwerk, 1980; Saether, 1980; Runnells and Esmaili, 1981; Margheim, 1975; Fox, 1982; Metcalf and Eddy, 1975; Schmehl and McCaslin, 1973) and in field lysimeter investigations (Ward et al., 1971; Margheim, 1975; Ward and Reinecke, 1972; Metcalf and Eddy, 1975; Harbert and Berg, 1978; Kilkelly et al., 1981a). Some of the more relevant data for characterization purposes is summarized in Table 4-6. This body of work indicates that the major ions in TOSCO II leachates are usually Na and SO_4. Other major ions include Ca, Mg, Cl, HCO_3, and S_2O_3. The leachates have an initial pH of 8 to 9 which may subsequently drop to 3 to 5. The trace elements and ions that occur at concentrations greater than 0.1 ppm under most test conditions (excluding first pore volume) are NO_3, PO_4, Al, B, F, Mo, Sr, V, and Si. Molybdenum is notably high in TOSCO II leachates compared to other spent shales, ranging from 0.03 to 76 ppm. Other elements measured (Table 4-6) are in the ppb range or are below detection limits.

The chemical species in TOSCO II leachates have been studied using a computer equilibrium model (Stollenwerk, 1980) and by experimental techniques (Fox, 1982a). The results of Stollenwerk's calculations, shown in Table 4-7, indicate that the dominant aqueous form of B is the neutrally charged species,

TABLE 4-6

Inorganic Composition of TOSCO II Leachates Produced During Laboratory and Field Lysimeter Studies (mg/L).

	LABORATORY STUDIES				FIELD LYSIMETER STUDIES			
	Batch (Runnells and Esmaili, 1981)	Batch (Runnells and Esmaili, 1981)	Column First Pore Volume (Stollenwerk, 1980)[a]	Blender (Margheim, 1975)	Rainfall Runoff (Margheim, 1975)	Snowmelt Runoff (Ward and Reinecke, 1972)	Rainfall Runoff (Metcalf) and Eddy, 1975)	Percolation (Metcalf and Eddy, 1975)
Al	7.6	20	≤0.1	-	-	-	0.06 - 0.2[b]	0.09 - 2
As	<0.2	0.6	0.02	-	-	-	0.005 - 0.008[b]	0.02 - 0.2
B	5.2	11.5	10	-	-	-	-	0.02 - 0.9
Ba	<0.02	0.017	-	-	-	-	0.02 - 0.04[b]	0.01 - 0.1
Br	<1	<1	1.3	-	-	-	0.02[b]	0.1 - 0.7
Ca	1.6	1.0	470	114	10 - 232	9 - 83	15 - 140	420 - 550
Cd	<0.02	<0.02	-	-	-	-	-	0.003 - 0.006
Cl	22	52	230	7.6	-	-	-	-
Co	<0.02	<0.02	-	-	-	-	0.01[b]	0.001 - 0.07
Cr	<0.01	<0.01	0.12	-	-	-	0.01[b]	0.003 - 0.009
Cu	0.03	<0.01	0.08	-	-	-	0.02[b]	0.06 - 0.2
DOC	96	-	73	-	-	-	-	-
EC (μmhos/cm)	-	-	-	1750	88 - 1415	58 - 572	300 - 1800	-
F	76	155	26	-	-	-	1.5 - 24	5.2 - 18
Fe	<0.01	≤0.02	0.24	-	-	-	0.1 - 0.3[b]	<1 - 8
HCO_3	-	-	390	20	20 - 25	13 - 89	-	-
Hg	<0.05	≤0.06	-	-	-	-	0.00002 - 0.00007[b]	<3x10^{-6} - 5x10^{-4}
K	8	10.6	77	32	-	<0.1 - 1.8	4.3 - 33	59 - 140
Li	<0.1	0.2	-	-	-	-	0.02[b]	0.007 - 0.8
Mg	0.4	<0.3	1700	27	<0.6 - 16	0.9 - 22	13 - 23	64 - 315
Mn	<0.01	<0.01	0.42	-	-	-	0.004[b]	0.06 - 0.5
Mo	3.2	6.3	3.9	-	-	-	0.03[b]	3 - 76
Na	815	1865	4700	165	<1 - 74	0.2 - 11	35 - 518	7820 - 17,825
Ni	<0.02	<0.02	<0.04	-	-	-	0.02 - 0.05[b]	0.05 - 0.6
NH_4	2	≤2	7.7	-	-	-	-	-
NO_3	3	3	<0.2	5.6	-	-	-	-
NO_2	<0.5	<0.5	<0.1	-	-	-	-	-
Oil and grease	-	-	-	-	-	-	7 - 18	50 - 163
Pb	<0.1	<0.1	<0.03	-	-	-	-	0.003 - 0.004
PO_4	<1	3	0.18	-	-	-	-	-
Rb	-	-	0.18	-	-	-	0.004 - 0.03[b]	0.01 - 0.03
S	530	1300	-	-	-	-	-	-
Sediment	-	-	-	-	1300 - 5500	-	1790 - 27,450	14 - 120
Se	<0.3	<0.3	0.02	-	-	-	0.004 - 0.007[b]	0.4 - 2
Si	0.12	1.4	6.5	-	-	-	0.3 - 1[b]	4 - 8
SO_4	625	1700	15,700	730	7 - 726	16 - 239	-	29,110 - 31,120
Sn	<0.15	≤0.18	<0.06	-	-	-	-	0.003 - 0.005
Sr	0.07	0.05	9.8	-	-	-	0.2[b]	4 - 6
TDS	2185	5480	23,680	1262	-	-	243 - 4518	28,425 - 57,137
TOC	-	-	-	-	-	-	2 - 10	284 - 647
U	<0.5	<0.5	-	-	-	-	-	-
V	0.12	0.61	-	-	-	-	0.01[b]	0.003 - 0.01
Zn	<0.01	<0.01	≤0.03	-	-	-	0.01 - 0.09[b]	0.9 - 3
pH (units)	9.9	10.3	8.0	8.4	7.74 - 8.52	7.58 - 8.95	7.4 - 8.15	2.5 - 4.8
Bulk density, g/cm^3	-	-	1.15	-	1.39	1.39	1.36	1.36
Solid-to-liquid ratio	0.4 g/ml	1.0 g/ml	2.8 g/ml	0.1 g/ml	0.46 - 1.0	<0.01 - 0.08	0.79	0.79
Contact time	17 days	17 days	46 days	5 min.	3.6 hours	1.4, 4.2 hrs.	20 min - 48 hrs.	-
No. of replicates	2	4	4	1				

[a] Samples collected and analyzed in quarter pore volumes. Recorded value is average for four samples collected over first complete pore volume.

[b] Average or range for two samples of runoff collected 16 and 48 hrs. after start of rainfall. Analyses by spark source mass spectrometry, except Hg, which is by flameless atomic absorption spectrometry.

TABLE 4-7

Chemical Species Present in First Pore Volume Leachates (see Table 4-6, Column 3) of Paraho Direct and TOSCO II Spent Shales Computed Using WATEQFC, a Chemical Equilibrium Model (Stollenwerk, 1980).

	Concentration (mm/L)[a]	
	Paraho	TOSCO II
Cl^-	14	16
$NaCl^o$	0.05	0.05
(Total Cl)	(14)	(16)
SO_4^{2-}	120	190
$NaSO_4^-$	44	58
$MgSO_4^o$	0.88	74
$CaSO_4^o$	7.6	6.1
$NH_4SO_4^-$	0.02	0.20
KSO_4^-	4.0	0.57
(Total SO_4)	(180)	(330)
HCO_3^-	0.46	7.0
$NaHCO_3^o$	0.04	0.56
CO_3^{2-}	0.26	0.11
$NaCO_3^-$	0.36	0.14
$MgHCO_3^+$	0.001	1.1
$CaHCO_3^+$	0.007	0.07
$H_2CO_3^o$	0.001	0.09
$MgCO_3^o$	0.01	0.27
$CaCO_3^o$	0.12	0.03
(Total HCO_3 + CO_3)	(2.4)	(9.9)
Ca^{2+}	6.1	4.2
$CaSO_4^o$	7.6	6.1
$CaCO_3^o$	0.12	0.03
$CaHCO_3^+$	0.007	0.07
CaF^+	0.005	0.008
(Total Ca)	(14)	(10)

	Concentration (mm/L)[a]	
	Paraho	TOSCO II
Mg^{2+}	0.75	52
$MgSO_4^o$	0.88	74
$MgHCO_3^+$	0.001	1.1
$MgCO_3^o$	0.01	0.27
MgF^+	0.006	0.92
(Total Mg)	(1.6)	(130)
Na^+	330	350
$NaSO_4^-$	44	58
$NaHCO_3^o$	0.04	0.56
$NaCO_3^-$	0.36	0.14
NaF^o	0.03	0.08
$NaCl^o$	0.05	0.05
(Total Na)	(380)	(410)
K^+	25	2.9
KSO_4^-	4.0	0.57
(Total K)	(29)	(3.5)
F^-	0.38	0.92
NaF^o	0.03	0.08
MgF^+	0.006	0.92
CaF^+	0.005	0.008
(Total F)	(0.43)	(1.9)
$B(OH)_3^o$	0.02	1.2
$B(OH)_4^-$	0.06	0.10
(Total B)	(0.08)	(1.3)
MoO_4^{2-}	0.03	0.06
(Total Mo)	(0.03)	(0.06)

[a] Millimoles/L

$B(OH)_3^0$. Fluorine is present as the free fluoride ion, F^-, and as the complex, MgF^+, while Mo is present as MoO_4^{2-}. Stollenwerk's calculations suggest that the concentrations of Mo and F in these leachates may be controlled by Ca; e.g., CaF_2 and $CaMoO_4$. Fox (1982a) found that the predominant As species in TOSCO II leachates are AsO_4^{3-} and methylarsonic acid.

The lysimeter studies have demonstrated that the composition of runoff and percolation are quite different. This is highlighted by the data summarized in Table 4-8. For a given precipitation event, surface runoff will contain orders of magnitude lower concentrations of dissolved solids (TDS, Na, Ca, etc.) than percolation (Metcalf and Eddy, 1975). This is probably due to the shorter contact time and smaller interfacial areas between the water and shale during runoff. The concentration of dissolved substances in runoff decrease exponentially to very low levels, 1 to 10 ppm, several minutes into a runoff event (Margheim, 1975; Ward and Reinecke, 1972). Thus, the higher runoff concentrations summarized in Table 4-6 occur early in a precipitation event, while the lower concentrations occur later. Although the lysimeter work on TOSCO II spent shale (Metcalf and Eddy, 1975) has not shown a similar decrease with time for percolation, other longer term studies using Paraho spent shale (Wildung et al., 1980-82; Garland et al., 1979) have shown similar decreases. Table 4-6 also indicates that the chemical quality of runoff from rainfall and snowmelt is similar.

Field lysimeter studies also have revealed that a salt deposit may form on the surface of TOSCO II spent shales (Margheim, 1975; Harbert and Berg, 1978; Runnells and Esmaili, 1981) which affects runoff quality. They are formed by the capillary movement of concentrated salt solutions to the pile surface followed by rapid evaporation (Harbert and Berg, 1978). Laboratory studies indicate that these salts are very soluble (Margheim, 1975; Runnells and Esmaili, 1981), and lysimeter studies indicate that they are removed during the first spring thunderstorms, resulting in high salinity in initial runoffs, especially if runoff volumes are low (Harbert and Berg, 1978; Kilkelly et al., 1981a). X-ray diffraction analyses indicate that these salts are chiefly sodium sulfate (Runnells and Esmaili, 1981), and other work indicates that their leachates contain high concentrations of Na and SO_4, and elevated, but lesser amounts of Ca, Mg, and F (Margheim, 1975; Runnells and Esmaili, 1981). There is some evidence that these deposits can be controlled by soil cover and preleaching (Harbert and Berg, 1978; Kilkelly et al., 1981a). However, without special treatment, they may continue to form for years (Runnells and Esmaili, 1981).

Lysimeter studies also have revealed that the pH of percolates decreases from initial values of 8 to 9 to final values of 2 to 3 within a few weeks of sample collection. Similar pH changes have not been observed for surface runoff (Metcalf and Eddy, 1975). Percolation pH changes have been observed for TOSCO II spent shale (Metcalf and Eddy, 1975) and Paraho spent shale leachates (Garland et al., 1979; Stollenwerk, 1980). Metcalf and Eddy (1975) also noted that the pH change was accompanied by a color change from yellow to blue or blue-green. They hypothesized that this was due to the reduction of hexavalent Mo to the molybdenum blue complex that occurs in the presence of acid and polythionates.

TABLE 4-8

Comparison of Average Quality of Runoff and Percolation From Two Separate Simulated Rainfall Events (0.79 in/hr 8 hr/day for Several Days) in Field Lysimeters of Compacted (1.36 g/cc) TOSCO II Spent Shale (Metcalf and Eddy, 1975).

	Na (mg/L)	Suspended Solids (mg/L)	Total Dissolved (mg/L)	pH
TEST 1				
Runoff	40	4,600	520	7.8
Percolation	10,500	50	41,500	2.6
TEST 4				
Runoff	55	--	--	8.1
Percolation	10,400	--	--	2.6

Stollenwerk (1980) demonstrated that the pH drop is probably due to the oxidation of thiosulfate to elemental sulfur and sulfuric acid by bacteria. He proposed the following reaction pathways:

$$5S_2O_3{}^{2-}\ (aq) + H_2O + 4O_2(g) \xrightarrow{\text{T. thioparus}} 6SO_4{}^{2-}\ (aq) + 2H^+\ (aq) + 4S^o(s)$$

$$2S(s) + 3O_2(g) + 2H_2O \xrightarrow{\text{T. thiooxidans}} 2H_2SO_4(aq)$$

Brierley and Brierley (1981) have studied 30 samples of spent and raw shale and their leachates for the presence of thiosulfate-oxidizing microorganisms using enrichment and selective media techniques. Preliminary results demonstrate that the potential does exist for microbial thiosulfate oxidation.

Different laboratory techniques result in significant differences in TOSCO II leachate quality. This is evident from examining the four laboratory samples in Table 4-6. (The reasons for these differences will be discussed in the Mechanism Section.) In general, the blender technique used by Margheim (1975) produced leachate concentrations that are similar to the maximum runoff concentrations measured in field tests while for column studies, the first pore volume (Stollenwerk, 1980) is similar to ranges reported for initial lysimeter percolation (Metcalf and Eddy, 1975).

Different samples from the same process also may yield different quality leachates. Runnells and Esmaili (1981) analyzed three separate samples of TOSCO II spent shale that spanned several years of retort operations. They noted some interesting differences among the three. A fresh sample (SS-4) had a significantly higher pH and F concentration and a lower Ca concentration than the others. They hypothesized that this was due to nahcolite in the fresh sample. Bicarbonate from this mineral would remove Ca by precipitation. And, since Ca controls F solubility (CaF_2), higher F concentrations would result.

There was also a factor of two difference in the concentration of Mo in leachates from two other samples (SS-1 and SS-2). These types of differences point to the need for a systems approach to leachate study. The relationship between raw shale mineralogy, retorting conditions, spent shale mineralogy, and leachate quality should be established in such studies.

Paraho Direct-Mode

The inorganic composition of Paraho leachates has been studied using laboratory column and batch studies (Holtz, 1976; Silviera et al., 1978; Cleave et al., 1979; Stollenwerk, 1980; Saether, 1980; Runnells and Esmaili, 1981; Fox, 1982) and in field lysimeter investigations (Harbert et al., 1979; Garland et al., 1979; Wildung and Zachara, 1981; Kilkelly et al., 1981c; Malek, 1981). These studies have used both indirect-mode and direct-mode spent shales. This section will discuss only the composition of direct-mode Paraho leachates.

Some of the more relevant data from these studies for characterization purposes are summarized in Table 4-9. This work indicates that the major ions in Paraho leachates are Na and SO_4, and they constitute well over 50% of the total dissolved salts. Other major ions include Ca, Mg, K, and HCO_3. High concentrations of S_2O_3 also occur under some test conditions (Garland et al., 1979; Stollenwerk, 1980). The leachates have a pH of 9 to 11. Values as high as 11.7 have been measured in field lysimeter percolates. This range in pH is related to differences in spent shale and leachate sample collection and preservation methods. Stollenwerk (1980) noted that the pH of Paraho leachates depends on spent shale age due to atmospheric recarbonation of lime. Fresh samples tend to produce high pH leachates, around 11, while older samples have pHs of 8 to 9. In other work, Taylor et al. (1982) observed that the pH of leachates from laboratory spent shale containing 23% CaO remain in the range of 12.3 to 12.7 in the absence of air, and the Ca reaches 450 mg/L. In the presence of air, the pH falls to 9.9 in 72 hours, and the Ca drops to 18 mg/L. These effects are due to well known recarbonation reactions, as follows:

Recarbonation of Spent Shale

$$CaO + CO_2(g) \rightleftharpoons CaCO_3(s)$$

Recarbonation of Leachates

$$H_2O + CO_2 \rightleftharpoons CO_3^{=} + 2H^{+}$$

$$Ca^{+2} + CO_3^{-2} \rightleftharpoons CaCO_3(s)$$

Others have noted that the pH of field leachates may drop as low as 7 after a year of weathering (Garland et al., 1979; Harbert et al., 1979; Kilkelly et al., 1981c). This is probably due to oxidation of thiosulfate by a mechanism similar to that previously discussed for TOSCO II spent shales (Garland et al., 1979; Stollenwerk, 1980). Similar drops in pH have not been observed in laboratory studies of Paraho spent shale.

The trace elements that occur at concentrations greater than about 0.1 ppm under most test conditions include B, Ba, F, Li, Mo, Rb, Si, Sr, and V. Other elements studied to date (Table 4-9) are in the ppb range or are below detection limits. Lithium in lysimeter percolates was present at concentrations

TABLE 4-9

Inorganic Composition of Paraho Direct-mode Spent Shale Leachates Produced During Laboratory and Field Lysimeter Studies (mg/L).

	Batch Utah Shale (Cleave et al., 1979)	Column Utah Shale (Cleave et al., 1979)	Column Colorado Shale[c] (Stollenwerk, 1980)	Lysimeter[d] Percolate Colorado Shale (Garland et al., 1979)	Lysimeter[d] Runoff Colorado Shale (Kilkelly et al., 1981[c])
Al	-	-	≤0.1	0.0005 - 0.1	-
As	0.010	<0.001[b]	0.04	0.007 - 0.08	-
B	0.25	0.015[b]	0.6	0.5 - 3	-
Ba	0.14	0.21[b]	-	0.03 - 0.55	-
Br	-	-	0.16	-	-
Ca	654	172 - 466	480	140 - 530	7 - 10
Cd	<0.013	0.021[b]	-	-	-
Cl	30	1.1 - 3.0	220	70 - 2200	<4
CO_3	15	0	-	-	0
Cr	0.011	0.015[b]	0.06	<0.001 - 0.02	-
Cu	<0.011	0.016[b]	0.04	<0.001 - 0.07	-
DOC	-	-	24	<2 - 400	-
EC (µmhos/cm)	6415	1007 - 10,230	-	8000 - 30,000	70 - 170
F	-	-	6.4	3 - 13	-
Fe	<0.025	0.028[b]	0.08	<0.01 - 0.3	-
HCO_3	180	133 - 1,483	80	-	18 - 50
K	55	8 - 455	640	320 - 1230	4 - 5
Li	-	-	-	6 - 20	-
Mg	246	24 - 317	33	0.2 - 140	3 - 14
Mn	<0.007	0.016[b]	<0.01	<0.01 - 0.075	-
Mo	-	-	1.5	1.2 - 9.5	-
Na	822	22 - 2740	4000	1500 - 10,400	2 - 5
Ni	-	-	<0.03	<0.005 - 0.04	-
NH_4	-	-	1.4	<1 - 11	-
NO_3	-	-	<0.2	<0.1 - 6	-
NO_2	-	-	0.36	0.001 - 4	-
Pb	<0.001	0.049[b]	<0.02	-	-
PO_4	-	-	0.09	-	-
Rb	-	-	2.2	-	-
Se	<0.001	0.0022[b]	0.07	0.0005 - 0.04	-
Si	-	-	10	5 - 16	-
SO_4	4301	482 - 6600	8600	3000 - 20,000	5 - 14
Sn	-	-	<0.02	<0.04	-
Sr	-	-	6.8	4 - 13	-
TDS	7056	-	14,220	-	-
TOC	2	-	-	<2 - 429	-
U	-	-	-	<0.0003 - 0.003	-
V	-	-	-	0.1 - 0.45	-
Zn	0.013	0.056[b]	<0.02	0.005 - 1.1	-
pH	8.84	7.17 - 8.27	9.5	6.9 - 11.5	-
Bulk Density, g/cm^3	-	-	0.99	1.55	
Solid-to-liquid ratio, g/ml	0.1	-	2.2	-	
Contact time	30 min.	2.4 days	-	-	
Particle size (d_{50})	∿3 mm	∿3 mm	-2 mm	-	
No. of replicates	1	(a)	4	N/A	

[a] Range corresponds to six samples taken from t = 1.25 days to t = 12.3 days. The lowest value is usually for the 12 day sample, and the highest for the 1 day sample. The velocity through the column was ∿3×10^{-4} cm/sec.

[b] All trace element measurements for this column experiment were made at t = 1.25 days. See note (a).

[c] Samples collected and analyzed in quarter pore volumes. Recorded value is average for four samples, collected over first complete pore volume. Shale is same as in column (4) (Garland et al., 1979).

[d] Anvil Points lysimeter, high elevation site. Runoff values are for spring snowmelt. The first reported value for runoff is from spent shale with a 20-cm soil cover, and the second value is for runoff from preleached, bare spent shale.

that were 50 to 500 times greater than in leachates from surrounding soils, and well waters below the disposal pile at Anvil Points contained higher Li concentrations than well waters above the pile, indicating leachate migration into groundwaters (Wildung et al., 1981). This result suggests that Li may be a good tracer for Paraho leachates.

The chemical species in Paraho leachates have been studied using computer equilibrium models (Stollenwerk, 1980; Runnells and Esmaili, 1981) and by experimental techniques (Saether, 1980; Fox, 1982c). The results of Stollenwerk's calculations, shown in Table 4-7, indicate that the dominant aqueous form of B is the negatively charged species, $B(OH)_4^-$. Fluorine is present as the free fluoride ion, F^-, while Mo is present as MoO_4^{2-}. Saether (1980) verified the F distribution calculated by Stollenwerk (1980) using synthetic ion exchange resins. In other work, Fox (1982a) found that the major As species in Paraho leachates were AsO_4^{3-} and methylarsonic acid.

The lysimeter studies have revealed that chemical equilibrium between water and disposed shale is a slow process, requiring longer than four years and that major changes occur in the composition of percolates as a function of applied water volume and water residence time in the shale. These studies also have shown, as previously noted for TOSCO II spent shale, that the composition of runoff and percolation are very different.

Battelle-Pacific Northwest Laboratories (PNL) has been monitoring the chemical quality of percolate from the high-elevation CSU lysimeter (Harbert et al., 1979). Their preliminary data, summarized in Table 4-9, indicate a wide range in elemental composition of percolate water, and highlight the complexities of the natural environment. Their studies indicate that equilibrium is a very slow process in the field. Atmospheric recarbonation, oxidation, and microbial activity may play important roles in determining field leachate composition (Garland et al., 1979). They found that lysimeter spent shale was colonized by heterotrophic and anaerobic bacteria and by fungi and that their populations decreased with depth through the pile, suggesting that microbial activity may play an important role in leaching processes. Their work also generally validates the usual decrease in leachate concentrations observed in laboratory column studies (Malek, 1981; Silviera et al., 1978; Schmehl and McCaslin, 1973). However, recent measurements have revealed a pulse in the concentration of organic carbon, Cr, and Ni after three years of weathering (Figure 4-5). This is likely due to the as yet, poorly understood, complex succession of chemical and microbial changes that occur in the field (Wildung and Zachara, 1981). The elevated concentrations of Cr and Ni may be due to changes in redox state (Cr) or complexation reactions resulting from the increase in organic carbon. These types of occurrences point to the difficulty of studying the leaching phenomenon in the laboratory.

The laboratory studies summarized in Table 4-9 (and others not reported there) indicate that different laboratory techniques and samples result in significant differences in Paraho leachate quality. Briefly, the first pore volume of leachate reported by Stollenwerk (1980) and Cleave et al. (1979) reveal significant differences in leachates from Paraho shales produced from an Anvil Points and a Utah feedstock. In particular, there are order of magnitude differences in the concentration of Mg, HCO_3, and Cl. Similar differences are apparent in batch leaching studies in which the same methods were used and only the raw shale feedstock differed (see, for example, Table 4-16).

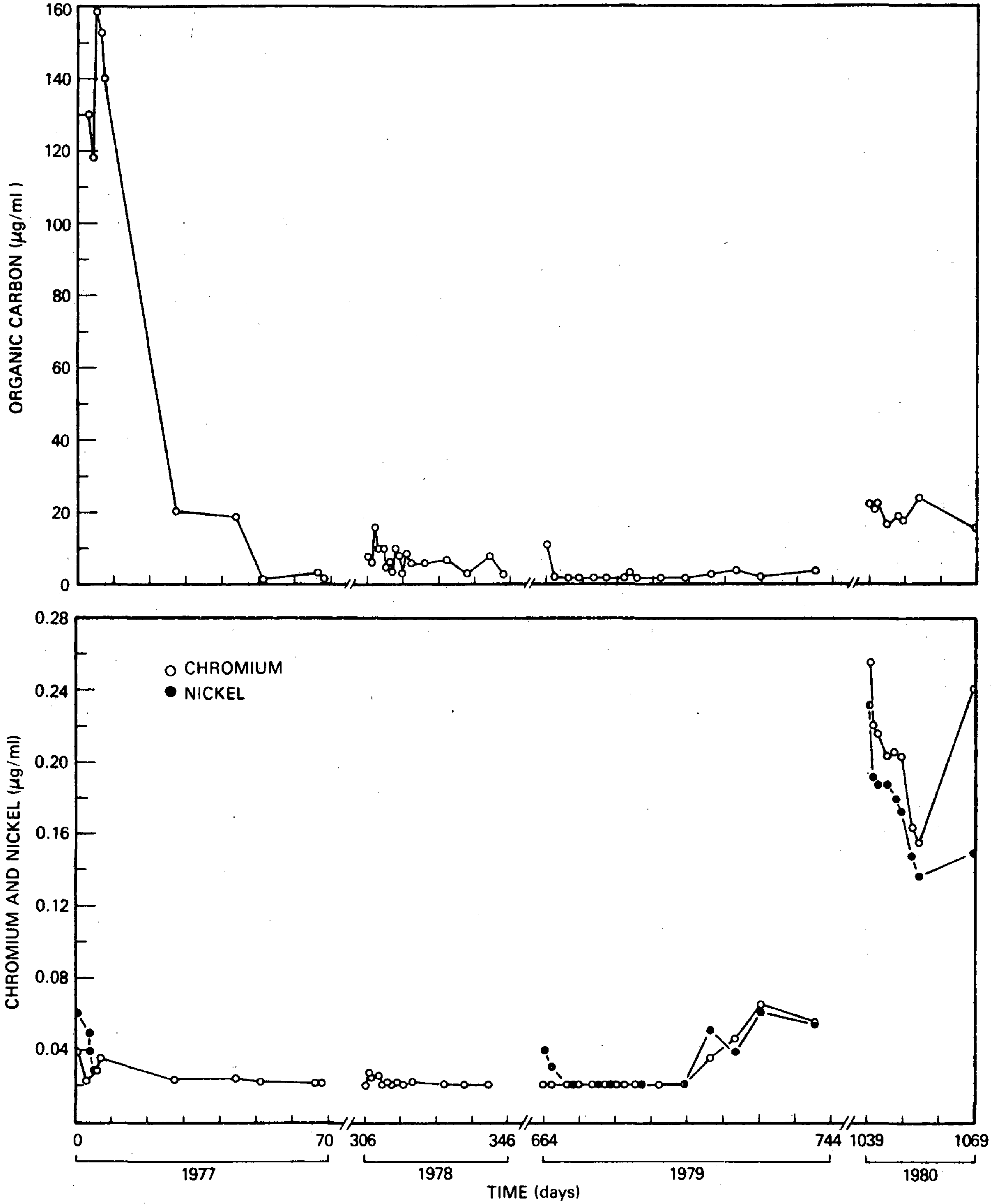

Figure 4-5. Concentrations of dissolved organic carbon, chromium and nickel in leachates from retorted shale in field lysimeters (unpublished).

Also, there are significant differences in leachate compositions produced by batch and column studies by the same investigator using the same sample (Cleave et al., 1979). These types of differences were discussed previously for TOSCO II leachates and will be explored in greater detail in the Mechanism Section.

Union

Only a few measurements of the quality of Union B leachate (Cleave et al., 1979; Union, 1979c), of Union A leachate (Margheim, 1975), and of Union SGR leachate (Herron et al., 1980) have been published. These studies (some are summarized in Table 4-10), reveal that there are significant differences in the quality of leachates from these three processes. However, the differences are consistent with retorting conditions and probable mineralogy, as discussed previously.

The major ions in Union B leachate are Na, Ca, HCO_3, and SO_4, and they constitute over 90% of the total dissolved salts. Other major ions include Cl, Mg, and K. Union B leachate has a pH of about 8, and the trace elements that occur at concentrations greater than 0.1 ppm are Al, B, F, Mo, and Sr. Separate measurements reported by Cleave et al. (1979) and Union (1979c) agree well, and the ionic balances for both leachates are excellent, closing to within 1% to 2%.

The Union A sample is more similar to other direct-mode processes, such as the Paraho direct process, than to indirect processes such as Union B. The Union A leachate has higher concentrations of TDS, Na, K, and SO_4 than Union B leachates and a higher pH. These differences are due to the higher temperatures and oxidizing atmosphere that occur during char combustion in the Union A retort.

Herron et al. (1980) reported measurements of EC, pH, and sediment in percolate and runoff from lysimeter studies of Union SGR spent shale. As noted for other spent shales (Paraho, TOSCO II), conductivity was lower in runoff (40-880 µmhos/cm) than in percolate (3600-10,000 µmhos/cm). Sediment was more variable, but generally low, especially from lysimeters with no soil cover. The pH of SGR percolate ranged for 9.5 to 12.1. There was no percolation through lysimeters with a soil cover over the spent shale, and coring revealed that a cemented layer had formed that apparently restricted downward movement of moisture. No such layer was observed in lysimeters without a soil cover. Similarly, runoff volume was greater from soil-cover plots than bare plots.

Superior

There is very little publicly available information on the leachability of solids from Superior's multimineral process. Only a single study has reported on the composition of leachates from Superior spent shale (Jackson and Jackson, 1982) and that data is summarized in Table 4-11. The trace element content of solids from the multimineral process, including raw shale, nahcolite, spent, unleached shale, and spent, leached and washed shale, are reported in NAS (1979).

TABLE 4-10

Inorganic Composition of Leachates From Two Types of Union Spent Shale (mg/L).

	Union B (Union, 1979c)	Union B (Cleave et al., 1979)	Union A (Margheim, 1975)
Ag	<0.02	<0.009	-
Al	0.2	-	-
As	0.004	<0.001	-
B	0.68	0.97	-
Ba	0.07	<0.078	-
Be	<0.01	-	-
Ca	95	243	327
Cd	<0.01	0.016	-
Cl	<2	7.0	33
CN	<0.01	-	-
Co	<0.1	-	-
CO_3	0	-	21
Cr	<0.005	<0.011	-
Cu	0.02	<0.011	-
EC (μmhos/cm)	750	-	11,050
F	6.1	-	3.4
Fe	<0.05	<0.025	-
HCO_3	25	172	28
Hg	0.0005	-	-
K	2.5	7.4	625
Li	0.09	-	-
Mg	24	58	91
Mn	0.02	<0.007	-
Mo	0.4	-	-
Na	130	109	2100
Ni	<0.04	-	-
N, Kjeldahl	0.6	-	-
NH_3-N	<1.0	-	-
NO_3	<10	-	-
NO_2	<5	-	-
Oil and grease	6	-	-
Pb	<0.05	0.009	-
Phenols	<1	-	-
PO_4	<10	-	-
$S^=$	<0.1	-	-
Se	<0.005	<0.001	-
SO_4	570	878	6230
Sr	1.2	-	-
TDS	800	1518	10,011
TOC	<1	11.3	-
V	<0.03	-	-
Zn	0.02	0.025	-
pH	7.7	8.33	9.94
Particle diameter	-	-	-40 mesh
Solid-to-liquid ratio (g/mL)	0.1	0.1	0.1
Contact time (min)	5	30	5

TABLE 4-11

Inorganic Composition of Superior Leachate Produced by the ASTM Test Method D3987 (Jackson and Jackson, 1982).

Element	Concentration[a] (mg/l)
Ag	<0.1
As	<0.1
B	0.16 - 0.22
Ba	<0.1
Cd	<0.1
Cl	>5
Cr	<0.1
EC (μmho/cm)	2400 - 3250
Li	0.51 - 0.80
Mn	<0.1
Mo	0.39 - 0.46
NH_3	0 - 2
Ni	<0.1
Pb	<0.1
Se	0.14 - 0.20
SO_4	896 - 1908
Sr	0.33 - 0.58
Th	0.43 - 0.56
TOC	>20
pH	9.4

[a] Samples were prewetted to 20 wt% with distilled water, compacted, equilibrated for 0 to 4 weeks, fractured, and leached by ASTM D3987. In this test, 350 g of solid are leached in 1.4 liters of distilled water and the leachate diluted to 2 liters prior to analysis. Chemical analysis was by inductively coupled argon plasma spectrometry and other methods.

Since analyses have not been reported for most major ions, it is difficult to contrast these results with other processes. However, based on the sulfate and pH levels, it appears that the Superior leachate is more similar to other indirect process leachates than to Paraho leachates (Table 4-5). The trace elements that occur at concentrations greater than about 0.1 ppm include B, Li, Mo, Se, Sr, and Th. High levels of Th and Se were not noted in other spent shale leachates, and the cause for this difference is unknown.

Additional work should be conducted to determine the composition of leachates from the various solids produced in the multimineral process. Particular attention should be focused on drained slurries similar to those that will be disposed, rather than on spent shale discharged from the retort. (The origin of the sample studied by Jackson and Jackson (1982) is unknown.)

Organic Composition of Surface Leachates

A number of studies (Tables 4-6, 4-9, and 4-10) has demonstrated that water-soluble organics are present in surface spent shales, and measured leachate organic concentrations range from 1 to 650 ppm. These organics probably originate from sorbed pyrolysis and recycle gases and unvolatilized kerogen decomposition products.

The organic content of leachates from surface spent shale is important due to the inherent toxicity and carcinogenicity of some organic compounds and due to possible interactions between organics and metallic ions. Some organics, particularly the organo-nitrogen compounds and carboxylic acids which are common in many oil shale effluents (Fish, et al., 1981; Raphaelian and Harrison, 1981), may complex metal ions, increasing their mobility. Or organics may deplete oxygen, lowering the Eh of leachates and, thus, affect the redox state and mobility of ions such as Cr and Fe. Evidence that these or other types of interactions between organics and metals occur under natural conditions has been accumulated (Wildung and Zachara, 1981; Stanley et al., 1981).

Available data on the leaching of organics from surface spent shales is reviewed here. This has been studied by Schmidt-Collerus et al. (1976); Wapensky (1976); Caolo et al. (1981); Maase (1980; Prien et al. (1977); and Carpenter (1978). (An expanded version of the Schmidt-Collerus work was reported by Bonomo (1974) and will also be reviewed.) Other, less extensive investigations, have been conducted in conjunction with other work (Metcalf and Eddy, 1975; Riley et al., 1981). Most of these studies have used exhaustive solvent (and, water) extractions in Soxhlet apparatuses to separate the organics from the shale matrix so they can be concentrated and identified. The conditions used in these studies are not similar to those that would occur during leaching and many of the extracted compounds are insoluble or sparingly soluble in water. The very low concentrations of organic carbon in spent shale leachate make quantitative extraction and identification of compounds in this matrix exceedingly difficult. The majority of these studies has focused on the characterization of polycyclic aromatic compounds in benzene extracts of Paraho and TOSCO II spent shales. These studies have broadly demonstrated that the quantity and nature of organics in surface spent shales depend on the specific processing conditions and on sample age and handling. The data reveal a significant problem with post-retorting oxidation and other chemical changes which alter the nature of spent shale and leachate organics. With those caveats, the results of some characterizations of spent shale organics are presented.

TOSCO II

The concentration of organics in spent shale leachates depends on how the leachates are generated. The summary of TOSCO II leachate data in Table 4-6 indicates that surface runoff from TOSCO II spent shale piles will contain relatively low TOC concentrations, 2 to 10 ppm, while percolation will contain an order of magnitude more TOC, 284 to 647 ppm. The concentration of organic carbon in leachates obtained during batch and column tests falls somewhere between these two extremes. In column studies, higher concentration occurs during the first few pore volumes and then stabilizes at low levels (∿1 ppm).

Several studies have identified specific organic compounds and classes of compounds present in TOSCO II spent shale and their leachates (Coomes 1976, 1979; Schmidt-Colerus et al., 1976; Carpenter, 1978; Wapensky, 1976; Caolo et al., 1980). The results from these studies agree qualitatively though there are some notable differences related to sample age and storage conditions. The majority of the extractable organics (95%) are polar, and only small amounts are nonpolar in nature. Very little of this organic material is soluble in water. Oxygenated hydrocarbons predominate in aged samples and lower concentrations of alkanes, alkenes, and carboxylic acids are present. Normal hydrocarbons predominate in fresh samples. The quantitative results, however, differ greatly due to analytical methods, differences in processing conditions experienced by various samples, and differences in sample preservation and handling.

Carpenter has conducted the most complete investigation of extractable organics in TOSCO II spent shale. (Unfortunately, his sample was probably aged and poorly preserved.) He used an MP-3 thermal analyzer to determine that the total organic material in his sample was 0.45% (w/w). Successive Soxhlet extractions of 300 g with 800 ml of hexane, benzene, THF, and methanol for 36 to 48 hours revealed that 0.072 ± 0.008% (w/w) of this organic material (16% of total organics) was extractable. Thus, most of the organics in his samples of TOSCO II spent shale are insoluble in common solvents. Similar results have been obtained by many investigators for raw oil shale, and the insolubility of kerogen in common solvents has been used as an operational definition for kerogen. A second Soxhlet extraction in which 300 g shale was extracted for 48 hours with 1 L distilled water indicated that only 0.77% (10 ppm) of the spent shale organics are soluble in water. This is lower than, though consistent with, measurements of dissolved organic carbon in batch leachates summarized in Table 4-6. Caolo et al. (1980) also noted a much lower concentration of organics in a water extract of TOSCO II spent shale than in a comparable methylene-chloride extract.

Silica-column fractionation of the solvent-extractable organics revealed that about 1% of the total was low-molecular weight aliphatic hydrocarbons (eluted with hexane), about 5% ± 1% was nonpolar (eluted with benzene), and 95% ± 2% was polar in nature (eluted with methanol) (Carpenter, 1978). The predominance of polar material is consistent with results reported by

Metcalf and Eddy (1975). They found that a single sample of percolation water from a field lysimeter contained 33 mg/L bases, 52 mg/L acids, 30 mg/L phenols, and 75 mg/L "neutral" oils. Thus, 61% of their sample was polar material compared to 95% noted by Carpenter (1978). Differences in leachate sample production, spent shale sample history, and analytical techniques likely account for the difference.

Carpenter (1978) qualitatively identified the types of compounds present in the methanol and benzene extracts using GC-IR, GC-MS, HPLC and solid-probe MS. Gas chromatography on a Dexsil 300 column using IR for detection revealed that the methanol fraction contained predominately oxygenated hydrocarbons. Only about 10 major components were present, and phthalic acid esters were identified (Carpenter, 1978). Caolo et al. (1980) also identifed phthalate esters in Paraho aqueous extracts. These are possible contaminants from plastic containers. Prien et al. (1977), in analyses of Paraho direct and indirect spent shales, also found a predominance of oxygenated hydrocarbons in the benzene fraction. Carpenter (1978) has hypothesized that nonpolar hydrocarbons may have been converted to oxygenated polar derivatives during water cooling of the spent shale or by slow air oxidation during storage.

The benzene extract was found to contain principally elemental sulfur with small amounts of polycyclic aromatic compounds and only traces of nonvolatile hydrocarbons with molecular weights greater than 800 (Carpenter, 1978). Others (Maase, 1980; Metcalf and Eddy, 1975; Bonomo, 1974) also have found high concentrations of elemental sulfur in the benzene extract (which, incidentally, interferes with BaP determinations if not removed). The PAH compounds present in the benzene and water extracts were estimated to be, respectively, 0.13 ppm and <10 ppb (w/w) of the original spent shale by HPLC with fluorescence detection. These very low values for PAH content are orders of magnitude less than measured by Bonomo (1974).

The results of other analyses of benzene extractables are compared with Carpenter's in Table 4-12. It is important to note the wide range in benzene-extractable material reported by these investigators (0.004% to 0.24%). Schmidt-Collerus et al. (1976) hypothesized that the range in benzene-extractable material among their samples (he worked with one sample that was five years old on receipt and which had been stored in closed drums and a second sample which was six months old) was due to sample age. They argued that organics were either slowly lost by oxidation and/or by volatilization. The very low value of benzene extractables obtained by Carpenter (1978) (0.05 x 0.072% (w/w) = 0.004%) suggests that he worked with an aged sample. This is corroborated by the high concentration of oxygenated hydrocarbons in his sample. (No sample history is provided in his work.)

Other investigators have focused on identifying the specific compounds present in various extracts of spent shale or leachates. The benzene-soluble fraction of TOSCO II spent shale has been found to contain the C_{11} to C_{29} alkenes and alkanes (Maase, 1980) listed in Table 4-13 and polycyclic aromatic compounds including azarines, carbazoles, and high-molecular weight bases such as acridine and dibenz (a,j) acridine (Bonomo, 1974; Maase, 1980). Caolo et al. (1980) found that the major organics in a methylene-chloride extract of TOSCO II spent shale were saturated normal hydrocarbons, including the isoprene hydrocarbons, phytane and pristane.

TABLE 4-12

Summary of Benzene-soluble Organics (wt %) and BaP (ppb) Concentrations in Some Surface Spent Shale Samples.

Spent Shale Sample	Benzene-soluble Organics (weight %)				BaP in Benzene-soluble Organics (BaP in ppb)		
	(Maase, 1980)[a]	(Carpenter, 1978)[b]	(Bonomo, 1974)[c]	(Prien et al., 1977)[c]	(Bonomo, 1974)	(Coomes, 1976)	(Prien et al., 1977)
Union B	1.17	-	-	-	-	-	-
TOSCO II, fresh	0.19	-	0.24 ± 0.01	-	19 - 116	21 - 38	42
TOSCO II, several yrs. old	-	0.004 (<10 ppb)[d]	0.011 ± 0.005	-	-	-	-
Paraho Direct	0.016	-	-	0.03 (0.00)[d]	-	-	2
Paraho Indirect	5.0	-	-	2.15 (0.03)[d]	-	-	150

[a] 400g extracted with 1.2L benzene in a Soxhlet apparatus for 3 days.

[b] 300g extracted, in turn, with 800 ml of hexane, benzene, THF, and methanol for 36-48 hrs. each in a Soxhlet apparatus. The average percent extractable organics was 0.072% ± 0.008% and 5% of this was eluted with benzene in silica-column fraction of the extracted organics.

[c] 400g extracted with 500-ml double-distilled benzene in a Soxhlet apparatus for 6 days.

[d] Benzene-soluble organics in water extract of spent shale.

TABLE 4-13

Some Hydrocarbons Identified in the Benzene Extract of a TOSCO II Spent Shale Using Glass-capillary GC-MS (Maase, 1980).

Formula	Molecular Weight	Compound
$C_{11}H_{22}$	154	1-undecene
$C_{11}H_{24}$	156	Undecane
$C_{12}H_{24}$	168	1-dodecene
$C_{12}H_{26}$	170	Dodecane
$C_{13}H_{28}$	184	Undecane, dimethyl
$C_{13}H_{26}$	182	1-tridecene
$C_{13}H_{28}$	184	Tridecane
$C_{14}H_{28}$	196	1-tetradecene
$C_{14}H_{30}$	198	Tetradecane
$C_{15}H_{30}$	210	1-pentadecene
$C_{15}H_{32}$	212	Pentadecane
$C_{16}H_{32}$	224	1-hexadecene
$C_{16}H_{34}$	226	Hexadecane
$C_{17}H_{34}$	238	1-heptadecene
$C_{17}H_{36}$	240	Heptadecane
$C_{18}H_{36}$	252	1-octadecene
$C_{18}H_{40}$	254	Octadecane
$C_{19}H_{38}$	266	1-nonadecene
$C_{19}H_{40}$	268	Nonadecane
$C_{20}H_{40}$	280	1-eicosene
$C_{20}H_{42}$	282	Eicosane
$C_{21}H_{42}$	294	1-heneicosene
$C_{21}H_{44}$	296	Heneicosane
$C_{22}H_{44}$	308	1-docosene
$C_{22}H_{46}$	310	Docosane
$C_{23}H_{46}$	322	1-tricosene
$C_{23}H_{48}$	324	Tricosane
$C_{24}H_{48}$	336	1-tetracosene
$C_{24}H_{50}$	338	Tetracosane
$C_{25}H_{50}$	350	1-pentacosene
$C_{25}H_{52}$	352	Pentacosane
$C_{26}H_{52}$	364	1-hexacosene
$C_{26}H_{54}$	366	Hexacosane
$C_{27}H_{54}$	378	1-heptacosene
$C_{27}H_{56}$	380	Heptacosane
$C_{28}H_{56}$	392	1-octacosene
$C_{28}H_{58}$	394	Octacosane
$C_{29}H_{60}$	408	Nonacosane

Some of the specific PAH compounds that have been identified by various investigators were summarized by Coomes (1976; 1979) and are shown in Table 4-14. The concentration of BaP in TOSCO II spent shales has been found to range from 19 to 116 ppb (w/w) (see Tables 4-12, 4-14). The higher value has been questioned by Coomes (1976).

TABLE 4-14

Some Polycyclic Aromatic Hydrocarbons that Have Been Detected in the Benzene Extract of TOSCO II Spent Shale.

COMPOUND	TOSCO II[a]
Benzo(a)pyrene (BaP)	28-55
Alkyl I (BaP)	x
Alkyl II (BaP)	x
Benzo(ghi)fluoranthene	x
Benzo(e)pyrene	18-29
Perylene	3-9
Benzo(ghi)perylene	12-24
Anthanthrene	3-5
Pyrene	58-102
Fluoranthene	21-23
Benz(a)anthracene	27-45
Triphenylene	13-34
Phenanthrene	x
7, 12 - Dimethylbenz(a)anthracene	x
3-Methylcholanthrene	x
Coronene	5
Chrysene	30-35

[a] The quantitative values are from Coomes, 1979. The range corresponds to 0 through 2 alkyl substituents. An "X" in this column indicates that the compound has been detected (Coomes, 1976; Bonomo, 1974) but not quantitated.

In other work, Wapensky (1976) studied the carboxylic acids present in two three-year-old samples of TOSCO spent shale. The acidic fraction was isolated from the spent shale by alkali extraction and found to contain 53.2 ppm of organic acidic materials. This is consistent with an analysis reported by Metcalf and Eddy (1975) in which 52 mg/L of acids was found in lysimeter percolate of TOSCO II spent shale. Carboxylic acids were found to constitute 74% of Wapensky's acid fraction. The extract was identified by GC-MS to contain: n-C_7-C_{10} aliphatic, benzoic, various methyl substituted benzoic, isopropyl benzoic and methyl isopropyl benzoic, β-hydroxy aliphatic, and high molecular weight aliphatic acids. Dibasic acids were detected also, and evidence was presented for a methyl substituted aliphatic acid. The identified carboxylic acids were strikingly similar to, but not identical to, those previously reported in raw shale. Wapensky hypothesized that pyrolysis liberated the abundant carboxylic acids present in kerogen, and some were absorbed onto the spent shale during retorting. He also noted that organic material, in the presence of oxygen, ultraviolet radiation and water vapor, can undergo hydroperoxide oxidation and complex acidic and polar molecules can be created. Differences between his two samples, which were stored under different conditions, were attributed to this mechanism.

The potential environmental and health significance of these findings is presently uncertain. The presence of PAHs or BaP, a priori, does not prove that a material is carcinogenic. A series of animal bioassays (Schmidt-Collerus, 1974) indicated that life-long contact with spent shale did not significantly increase the frequency of tumor formation. In other biological testing programs (Coomes 1976, 1979), hairless mice used spent TOSCO II shale as their bedding material. These studies revealed that TOSCO II spent shale did not exhibit acute or chronic toxic effects, based on mortality and body weight; it was not carcinogenic to the intestinal tract, larnyx, or trachea where exposure had been severe. In other work, solvent and water extracts of TOSCO II spent shale were assayed for mutagenicity using the Ames test (Dickson and Adams, 1980). These tests failed to show evidence that mutagens could be extracted in aqueous leachates. However, the authors cautioned that these results are not conclusive nor final due to limitations of the experimental techniques and the small quantities of samples which are tested.

Paraho

Table 4-9 indicates that the concentration of dissolved organic carbon in Paraho direct-mode spent shale leachates may range from less than 2 ppm to 429 ppm. As for other surface spent shales and in situ spent shales, the higher concentrations occur during the first few pore volumes and subsequently level off to relatively low values. However, the Paraho Anvil Points lysimeter studies (Wildung and Zachara, 1981) indicate that long-term weathering effects, perhaps microbial activity, may result in subsequent pulses of organic carbon (see Figure 4-5). These pulses may lead to the solubilization of metals such as Cr and Ni due to changes in redox state or complexation.

Only one detailed investigation of the organics in Paraho spent shales leachates has been conducted (Prien et al., 1977). This study focused on the benzene-soluble fraction of Paraho raw shale and of spent shales from direct and indirect-mode processes. Caolo et al. (1980), Maase (1980), and Riley et al. (1981) also have reported some organic analyses of Paraho leachates.

The benzene-soluble fraction of direct-mode [(0.02%, 0.03% w/w)] and of indirect-mode [(5.0%, 2.2% (w/w)] spent shales as measured by Maase (1980) and Prien et al. (1977) agree reasonably well, considering that different samples with unknown histories and different analytical methods were used (Table 4-12). Distilled-water extractions using similar procedures indicate that none (0.00%) of the benzene-soluble organics of direct-mode spent shale are soluble in water. About 1% of the benzene-soluble organics from indirect-mode spent shale are soluble in water. This is consistent with results obtained by Carpenter (1978) for TOSCO II spent shale.

Prien et al. (1977) also characterized some of the organics in the benzene-soluble fraction. They reported that 43% of this extract was PAH material in direct-mode spent shale. Similarly, about 15% of the indirect-mode benzene extract and 16% to 22% of the raw shale extracts, were PAH material. The balance of the benzene-soluble fraction was reported to be other polar oxygenated compounds such as acids, phenols, amines, etc. Some of the polar oxygenated compounds that they identified are summarized in Table 4-15. They found that the BaP content of their samples was 2 ppm for direct-mode and 150 ppb for indirect-mode samples.

In other work, Caolo et al. (1979) tentatively identified naphthalene, methyl- and dimethylnapthalene, pristane, and phytane in Me_2Cl_2 extracts while Riley et al. (1981) found that 0.05 M $NaHCO_3$ leachates of direct-mode Paraho spent shale contained no detectable amounts of C_3 - through C_6 - alkylpyridines and total alkylpyridines. (The detection limit for their GC-MS technique was 0.002 - 0.003 ppm for C_3 - C_6 alkylpyridines and 0.03 ppm for total alkylpyridines.)

It is important to note the differences between direct- and indirect-mode Paraho spent shales. The direct-mode sample has two orders of magnitude less benzene-soluble material and BaP than the indirect-mode sample. Similarly, the types of compounds differ. The direct-mode sample has a larger fraction of PAH material while other polar oxygenated material predominates in the indirect-mode sample. This points to the importance of clearly specifying sample processing conditions.

The potential health and environmental significance of the organics in Paraho leachates has been addressed in two studies. Ames tests of aqueous direct-mode leachates from a Utah raw shale feed failed to show evidence of mutagenicity (Dickson and Adams, 1980). In other work, static 24-hour acute bioassays using fathead minnow larvae and D. pulicaria in which leachates from the CSU Paraho lysimeters were tested failed to show any toxicity (Bergman, 1980).

TABLE 4-15

Polar Oxygenated Organic Compounds That Have Been Identified in the Benzene Extract of Paraho Direct- and Indirect-Mode Spent Shales by Gas Chromatography. The Reported Concentrations Are for Paraho Indirect-Mode Spent Shale (Prien et al., 1977).

COMPOUND	CONCENTRATION (ppm)
Heptanoic Acid	0.26
Benzoic Acid	0.18
Octanoic Acid	0.39
o-Toluic Acid	-
m-Toluic Acid	0.60
p-Toluic Acid	0.60
Nonanoic Acid	0.70
2, 5 - Dimethylbenzoic Acid	-
3, 5 - Dimethylbenzoic Acid	-
Decanoic Acid	-
3, 5 - Dimethylbenzoic Acid	-
Isopropylbenzoic Acid	-
Trimethylbenzoic Acid	-
Tetramethylbenzoic Acid	-
β - Hydroxy Aliphatic Acid	-
Methylisopropyl Benzoic	-
Aliphatic Dibasic Acid (C_{18})	-

SURFACE SPENT SHALE LEACHING MECHANISMS

The formation and transport of surface spent shale leachates have been approached from both an experimental and theoretical standpoint. A few investigators have developed computer models of water movement across or through spent shale piles and of the quality of percolation and runoff (Ward et al., 1971; Ward and Reinecke, 1972; Margheim, 1975; Bloomsburg and Wells, 1978). Other more fundamental modeling work is in progress (Ramirez 1981, 1982; Wildung et al. 1977-1971; Bond et al., 1982). Most investigators, however, have studied these phenomena using experimental techniques, laboratory and field studies designed to measure the composition of leachates for a given set of conditions.

Modeling studies generally have used laboratory investigations to develop model input data and field studies to validate models. In most cases, the resulting models are applicable only to the specific spent shale and set of conditions studied. Additionally, these modeling studies have tended to focus on either water movement or solute transport or on runoff or percolation. These four are interrelated and a given rainfall event produces both runoff and percolation. And solute movement is inextricably related to water movement.

The experimentalist, on the other hand, has studied the effect of a range of variables, in the absence of a consistent theoretical framework, on the volume and quality of leachates. Generally, their data are useful for characterizing only the specific set of samples and for the specific set of conditions that they investigated. And finally, there has been very little interaction between the experimentalist and the modeler.

These factors have contributed to a wide range in reported leachate compositions and in disparate conclusions regarding issues such as percolation through piles. There is an urgent need for a unified approach to water and solute transport modeling and the supporting laboratory studies. A consistent framework that simultaneously considers runoff and percolation and water and solute movement needs to be developed.

This section first overviews the theoretical framework of water and solute transport in the pile environment. It discusses the modeling work that has been completed and reviews the experimental studies that have been conducted. A subsequent section reviews the mechanistic experimental studies which have been conducted.

Modeling Studies

Spent shale disposed of by surface techniques will be exposed to rainfall and snowmelt which may "runoff" of the pile surface or "percolate" through the pile. This was shown schematically in Figure 1-1. The equations which describe both runoff and percolation are based upon the law of continuity or mass balance. A change in moisture content or solute concentration at a given point must equal a loss or gain by diffusion, dispersion, or inputs. Such mass balance approaches have been used by several investigators to model runoff and percolation from spent shale piles.

Runoff

Ward et al. (1971), using a water and salt balance approach, developed an equation for the concentration of total dissolved solids (TDS) in runoff from a spent shale piles as

$$\frac{(C-Cp)\gamma}{K} = 2-\log_{10}(iLt) \quad (iLt < 100 \text{ in-ft}) \qquad (2\text{-}1)$$

where:

C = concentration of dissolved solids in runoff

Cp = concentration of dissolved solids in precipitation

K = constant mass transfer coefficient for a given storm event

$$\log_{10} K_m = \frac{0.754}{\varepsilon} + \frac{3(\Delta\omega)}{(\omega_s)}$$

γ = runoff intensity

t = time since beginning of precipitation

L = length of overland flow

ε = porosity

$\Delta\omega$ = deviation of surface moisture content from moisture content at saturation

They verified this model for snowmelt and rainfall runoff using a field plot of TOSCO spent shale.

In another study, Ward and Reinecke (1972) and Margheim (1975) developed a quasi-empirical model that estimates the concentration of dissolved solids in runoff from TOSCO spent shale. Starting with a model of laminar flow, and using field data from a plot of TOSCO spent shale, they found that:

$$C = \frac{1.14 \times 10^{-8}\ \rho(\mathrm{Sin}\theta)^{2/3}}{k(\gamma iL)^{2/3}} \exp\left(\frac{4.5\Delta w - t^{1/3}}{0.435}\right) \qquad (2\text{-}2)$$

where:

γ = kinematic viscosity

ρ = density of surface

θ = angle of overland flow surface

k = permeability

Thus, the maximum TDS concentration in runoff will be found when compaction is greatest, slopes are steep, drying has been extensive, runoff has just begun, the shale residue has a low permeability, runoff water temperature is high, rainfall intensity is low, and length of overland flow is short. The quantities having the greatest effect on runoff TDS are the extent of drying before rainfall and time since runoff began. Next in effect are the bulk density and permeability of the spent shale. Least important (but not insignificant) are slope of the surface, runoff water viscosity, rainfall intensity, and length of overland flow (Margheim, 1975).

Their model agreed well with that reported by Ward et al. (1971). However, they (Margheim, 1975; Ward and Reinecke, 1972) cautioned that this equation was based on data from only one slope and two different compactions, and they recommended further work on the effect of compaction and slope angle. We are not aware of any further work in this area. However, a considerable quantity of relevant field data has been generated since this equation was developed (Metcalf and Eddy, 1975; Harbert and Berg, 1978; Harbert et al., 1979, Kilkelly et al., 1981) which could be used to validate and extend it to new situations. This has not been done to our knowledge.

Percolation

Percolation, on the other hand, involves the moment of water and solute through porous media. All of the work conducted in this area has modeled the infiltration of rainfall. No studies have addressed the infiltration of snow melt which involves much longer contact times between the media and fluid.

The underlying physics and chemistry of fluid flow and solute transport have been studied for decades by many investigators. Wildung and Zachara (1981) recently overviewed the governing water and solute transport equations as they apply to spent shale piles. Their development is used here.

The flow of water through a spent shale pile may be described by the one-dimensional flow equation for unsaturated soils.

$$\overset{\mathbf{A}}{\frac{\partial\theta}{\partial t}} = \overset{\mathbf{B}}{\frac{\partial}{\partial z} D(\theta) \frac{\partial\theta}{\partial z}} - \overset{\mathbf{C}}{\frac{\partial k(\theta)}{\partial z}} \qquad (2\text{-}3)$$

where:

θ = volumetric water content
t = time
z = vertical distance in the pile
$D(\theta)$ = shale-water diffusivity
$K(\theta)$ = hydraulic conductivity.

This equation describes the rate of change of moisture content with time (A) as a function of water movement by diffusion (B) and convective flow (C).

The analogous equation describing one-dimensional solute transport is

$$\overset{\mathbf{A}}{\frac{\partial(S+\theta C)}{\partial t}} = \overset{\mathbf{B}}{\frac{\partial}{\partial z}\left(\theta Ds(v)\frac{\partial C}{\partial z}\right)} - \overset{\mathbf{C}}{\frac{\partial(vC)}{\partial z}} - \overbrace{Q_1 - Q_2 - Q_3}^{\mathbf{D}} \qquad (2\text{-}4)$$

where:

C = solute concentration
S = amount of solute sorbed by the shale matrix per unit volume
θ = shale-water content
Ds = hydrodynamic dispersion coefficient
v = pore water velocity.

This equation describes the rate of change of the total solute concentration in a pile (A) as a function of the quantity of the solute moved by diffusion with concentration attenuation by dispersion (B), the quantity moved by convection (C), and additional changes from various sources and sinks (D). These latter terms may incorporate mathematical discriptions of chemical and biological reactions.

These types of equations may be used to predict water and solute movement through a spent shale pile by dividing the flow region into appropriately small subregions and satisfying these equations for each subdomain. The resulting set of implicit equations is solved simultaneously for the average time derivative in each subdomain using numerical techniques (called the "model"). The solution to these equations is the flow and concentration of select dissolved species as a function of time and position in the pile. Several investigators have used this approach to study water and solute transport through spent shale piles (Bloomsburg and Wells, 1978; Ramirez 1981, 1982; Bond et al., 1982).

These equations may be used to predict solute transport by using a "mass-transfer" or a "geochemical" approach. The mass-transfer approach (Sherwood et al., 1975) is based on physical concepts while the geochemical approach (Jenne 1979, 1981) is based on chemical concepts. In the mass-transfer model, equilibrium exchange isotherms, which relate the amount of a given ion released into the water to the bulk concentration, are used in conjunction with porous media properties and other transport properties to predict solute concentrations. This approach does not require a detailed fundamental understanding of the chemical mechanisms responsible for mass transfer.

The basis of the geochemical approach, on the other hand, is rock-solute chemistry. These models require kinetic and thermodynamic data on the chemical and physical reactions that occur between the solid and liquid phases, and they typically include model subroutines that calculate solubility, speciation, adsorption, ion exchange, precipitation, and dissolution reactions. The large quantity of fundamental data, much of which is not available, and the types of solute measurements, many of which cannot be easily done with existing analytical techniques, have limited the wide-scale use of geochemical models. Both the mass transfer (Ramirez 1981, 1982) and the geochemical approach (Wildung et al., 1977-1981; Margheim, 1975) have/are being used to study solute movement through spent shale piles. The work published to date is overviewed here.

The chemical approach has been used for major ions in TOSCO II leachates by Margheim (1975) and for major ions in Paraho leachates by Fransway (1980). Battelle Pacific Northwest Laboratory (PNL) also is using the chemical approach to study Paraho leachates (Wildung et al., 1977-1981). They are using a modified version of the USGS WATEQ2 chemical model (Ball et al., 1979) which calculates concentrations for a wide range of major, minor, and trace species. Although the results of this effort have not been published, some of their preliminary studies and input data have been (Rouston and Li, 1980; Silviera et al., 1978).

Margheim (1975) developed a chemical model that predicts the concentration of TDS and the major ions Mg, SO_4, Na, and Ca as a function of volume of water for TOSCO II spent shale. He developed equilibrium relationships for ion exchange (Ca, Mg, Na) with the spent shale and solubility of $CaSO_4$ and used mass balances around infinitesimal elements to predict solute concentrations. His model results agreed well with column studies using TOSCO II spent shale (Figure 4-6).

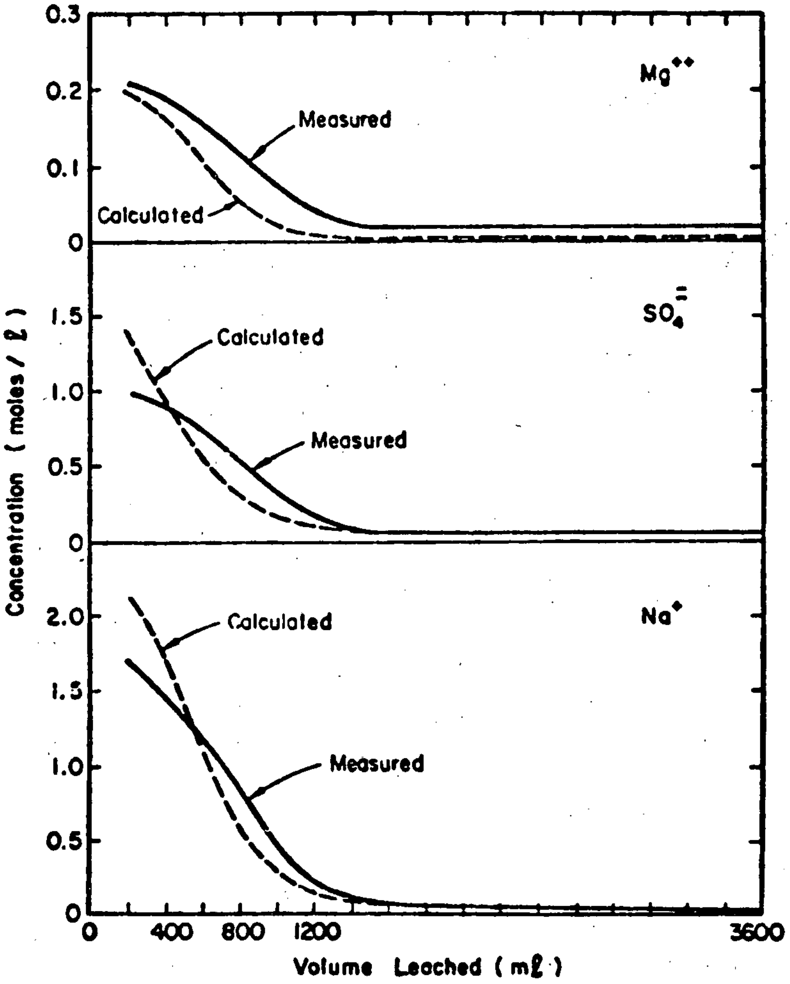

Figure 4-6. Model predictions and measured values of Na, SO_4, and Mg in leachate from columns of TOSCO II spent shale (Margheim, 1975).

In other similar work, Fransway (1980) used an existing chemical model to predict the concentration of EC and the major ions Ca, Mg, K, Cl, HCO_3, and CO_3 in percolates from Paraho direct-mode spent shale. The chemical subroutine calculates activities, ion pair formation for all species considered, and ionic strength, and it considers precipitation, ion exchange equilibria, and mineral dissolution. Model output includes water movement as a function of applied water volume and cumulative time and concentrations as a function of depth at selected points in a pile. Fransway (1980) validated his model with laboratory lysimeter data. He found good agreement for the water movement profile and for concentrations of Na and K. The model tended to overestimate EC during early time periods and to underestimate it during later time periods.

Ramirez (1981) is developing a mass-transfer solute-transport model which divides the flow region into a main channel area and a dead space volume area to account for the two distinctive types of porosity present in spent shale

(McWhorter, 1981a). He has determined the porosity, permeability, and specific surface area of TOSCO II and Paraho spent shales and developed equilibrium exchange isotherms for F, SO_4, CO_3, Ca, Mg, Na, B, and Sr. Other work is in progress to determine mass dispersion coefficients, mass transfer coefficients, and other porous media and transport properties. This information will be used in equations based on (2-3) and (2-4) to deterministically predict dynamic leachate behavior.

Investigators at the Battelle Pacific Northwest Laboratory (Bond et al., 1982) used a one-dimensional unsaturated groundwater flow code (UNSAT1D) to study the movement of water in spent shale piles. Infiltration, redistribution, and drainage of water from a Paraho spent shale pile were simulated for two test cases:

- an existing 35 m high pile
- a transient pile growing at a rate of 10 m/year for 5 yrs.

The first case simulated three different layering scenarios with each one run for 1 year. The second case simulated two different initial moisture contents (θ_i) in the pile (15% and near saturation). Moisture contents in this range may readily be reached when spent shale is moisturized to control dust and to facilitate compaction or if high intensity thunderstorms occur during pile construction. Each simulation was run for 30 years. Grand Junction and Rifle, Colorado, climatological data were used for precipitation and potential evapotranspiration for a wet (1979) and dry (1976) year. Plant water uptake was not simulated in either test case.

This study revealed that the principal parameters influencing drainage from the base of a pile are material hydraulic properties, material layering, and initial moisture content. This study suggests that water will move through a spent shale pile and drain from its base. The quantity of drainage will depend on the amount of infiltration into the pile while the time required before drainage occurs will depend principally on the initial moisture content. The initial moisture content of the pile influences the amount of storage in the embankment which, in turn, influences water movement into and drainage from the pile. At near saturation initial water levels, drainage occurred after the first year and continued for 30 years. After about 30 years, the pile approached an equilibrium state where the amount of drainage nearly equaled the amount of precipitation infiltrating at the surface. Precipitation alone did not result in drainage from the base of the embankment in 30 years for the pile initially at 15% (dry weight basis) water content. In this case, the remaining significant storage capacity extended the occurrence of drainage to beyond the 30 years simulated by Bond et al. (1982).

Bond et al. (1982) showed that permeability of shale at different compaction densities also will be an important factor influencing water movement in a spent shale embankment. Permeability at the surface regulates the amount of infiltration whereas permeability with depth regulates redistribution and drainage. Higher permeabilities at the surface may result in increased downward flux and in certain instances, increased upward flux due to evaporation. Lower permeabilities at depth may serve a useful purpose in restricting drainage but also may result in reduced storage capacity and perched water tables, depending upon circumstances.

In other work, Bloomsburg and Wells (1978) used an existing finite element model to study unsteady, unsaturated flow of water through a spent shale disposal pile. They conducted laboratory tests on Paraho direct-mode spent shale to determine model input parameters (porosity, saturated hydraulic conductivity, relative conductivity as a function of volumetric moisture content, and capillary pressure as a function of moisture content). The model was validated at the Anvil Points seepage ponds (Holtz, 1976), and it was used to study moisture movement through a spent shale pile for various boundary conditions. They analyzed the embankment in Figure 4-7 for three conditions:

- 100-yr, 1-hr storm (intensity of 0.95 in/hr)
- 100-yr, 6-hr storm (intensity of 0.25 in/hr)
- ponded condition (5 ft of water on the surface for 1 yr).

Their analyses suggest that infiltration will occur if water is ponded on the surface and that for climatic conditions existing in northwestern Colorado, infiltration of moisture into the piles is unlikely. They found that there was no runoff at any time during either storm for the 85-pcf shale and that there was runoff at all times for the 95-pcf shale. There was no saturated zone in the pile for either rainfall case. Moisture was held in the upper layer and subsequently assumed to evaporate. However, for ponding conditions, saturated zones developed (Figure 4-7). These investigators concluded that evaporation will completely remove water from low-intensity low-yield storms. High-intensity storms, however, may require an unconsolidated low-density surface layer such as proposed by Union (1979) to contain water until it is evaporated.

The work of Bond et al. (1982) and Bloomsburg and Wells (1978) do not agree on the occurrence of drainage from a spent shale pile. The work of Bloomsburg and Wells (1978), which suggests that drainage will not occur under anticipated conditions, agrees with moisture profile measurements at the Colony spent shale embankment (Heley, 1976) and with some lysimeter studies using TOSCO II spent shale (Harbert and Berg, 1978; Kilkelly et al. 1981a, 1981b). However, other field and modeling studies have demonstrated that under certain conditions, significant water movement occurs (Harbert et al., 1979; Kilkelly et al., 1981b; Garland et al. 1979; Bond et al., 1982). These differences are likely due to differences in modeling assumptions and experimental conditions. Since spent shale piles have not been built, we do not have definitive data to address these discrepancies, and additional work is required to resolve the drainage issue.

Experimental Studies

Many leachate investigations have used laboratory or field techniques to measure leachate composition for a given set of conditions. These studies, rather than developing "characterization" data per se, have taken a mechanistic approach and have focused on variables that control the composition of leachates. This occurred due to uncertainties surrounding spent shale disposal, including absence of definitive information on procedures that will be used in a commercial industry and absence of representative samples;

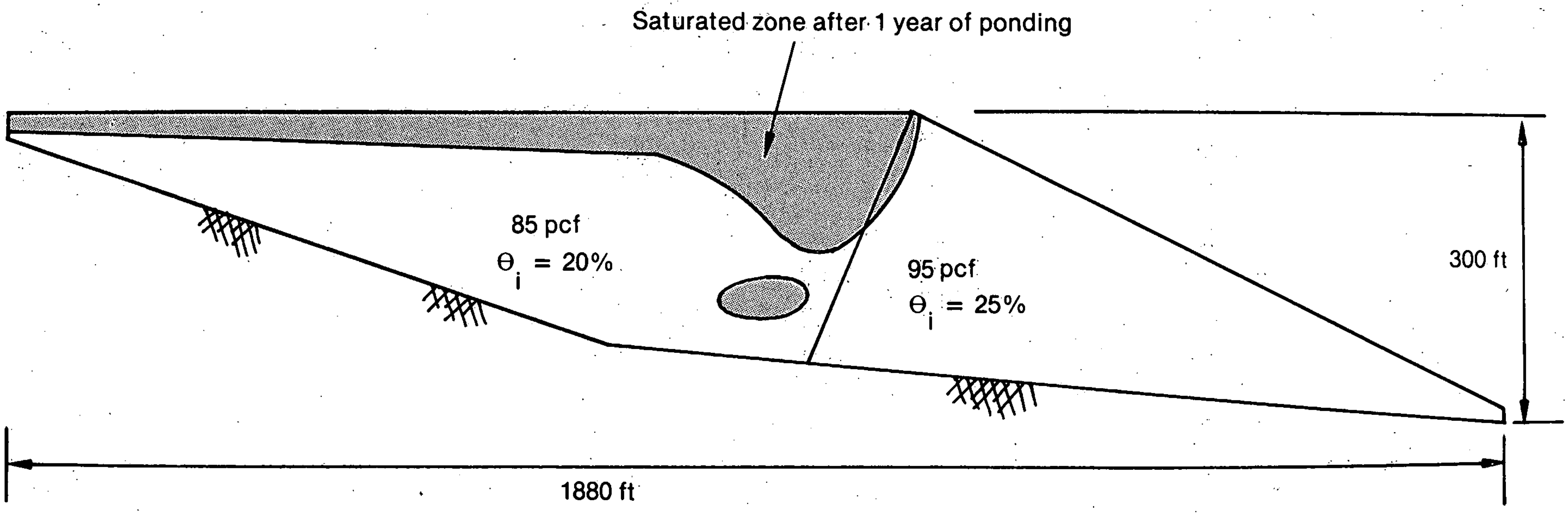

Figure 4-7. Typical cross-valley fill and simulated saturated zone after 1 year of ponding (Bloomsburg and Wells, 1978).

due to the complexity of the spent shale-natural environment system; and due to the absence of a conceptual framework of the leaching process. This focus on mechanisms has, in part, contributed to the wide ranges reported for leachate compositions, as is evident from Tables 4-6, 4-9, and 4-10.

The leaching of inorganic and organic material from surface spent shales is a complex physico-chemical process that is biologically mediated and which is subject to the vagaries of nature. The quality of these leachates depends on a large number of primary variables, process-related or environmental conditions, that affect fundamental physical, chemical, and biological processes. Some of the more important of these primary variables are:

Retorting Conditions

- raw shale composition
- atmosphere
- char gasification technology

Codisposal Methods

- quantity and composition of codisposed solids and liquids

Pile Design

- compactive effort
- face slope
- drainage control system
- erosion control measures

Reclamation Procedures

- plant cover
- soil depth and type
- capillary barrier

Climate

- ambient temperature
- freeze-thaw cycles
- wet-dry cycles
- rainfall volume, intensity, and timing
- snow depth
- chemical quality of precipitation.

These primary variables control secondary variables such as particle size, permeability, solid-to-liquid ratio, and redox conditions which drive the underlying physical, chemical, and biological interactions of leaching. Researchers have been studying the effect of these primary and secondary variables on leachate quantity and quality for a decade using a variety of laboratory and field techniques. This work has contributed to our understanding of fundamental processes, it reveals trends that may be expected in a commercial industry, and it has taught us how to design and revegetate piles to reduce leachate production. However, it has not provided information that allows the prediction of environmental impacts.

We will overview this work, organizing it by primary variables -- retorting conditions, codisposal methods, pile design, etc. -- and by secondary variables.

Raw Shale Mineralogy and Retorting Conditions

The composition of leachate ultimately depends on the mineralogy of the raw shale and retort operating conditions including temperature and atmosphere. This topic is exhaustively discussed for in situ leachates in Chapter 5. Most of the data from these studies (Peterson et al., 1982; Bethea et al., 1981; Park et al., 1980) are not directly applicable to surface processes. However, some of the lower temperature experiments (500 - 700 C) reported by Peterson et al. (1982) provide reasonable simulations for some surface processes. Thus, the interested reader is referred to that section.

Richardson (1979) reported some data on the effect of various raw shale feedstocks on Paraho spent shale leachates. [This data also is reported in Heistand et al. (1980)]. Their data, which are summarized in Table 4-16, reveal important differences for leachates produced from six different feedstocks. In general, the Colorado shales show higher concentrations of the major ions Na, K, Ca, Mg, and SO_4 and lower concentrations of HCO_3 than the single Utah sample. No information is presented on the mineralogy of the Colorado samples and thus, interpretations of these differences are not possible.

Very little research has been conducted on the effect of surface retorting conditions on leachate quality. The first such study investigated the effect of spent shale char combustion on leachate composition (Culbertson et al., 1970). They combusted the char on TOSCO spent shale in a solids burner (0.6 sec) and in a laboratory rotating-bed burner (0.5 to 2 hrs) at various temperatures. The resulting solids were batch leached (0.1 g/mL) for successive two to three day periods and 100-mL batches of leachate were analyzed for Ca, Na, K, Mg, Al, and Fe. They only reported results for Ca and Na, and some of these are plotted in Figure 4-8. This study showed that char oxidation increases the concentration of Ca and Na in leachates for all conditions tested, compared to unburned TOSCO spent shale. The Ca leachate concentration goes through a maxima around 800 C as also reported by Park et al. (1980). Longer char residence times tended to reduce the concentration of Ca for higher oxidation temperatures (816 C; 927 C) and to increase the concentration of Ca for lower temperatures (704 C). These results are consistent with the carbonate reactions that occur during retorting (see Figures 4-2, 4-3) and with later work by Taylor et al. (1982). The higher concentrations of Ca in leachates from combusted samples result from the formation of CaO during char oxidation and its hydrolysis during leaching. The observations on the effect of char residence time are consistent with Park et al. (1979)'s work (Figure 4-3).

TABLE 4-16

The Effect of Different Raw Shale Feedstocks on the Composition of Leachates From Paraho Direct-Mode Spent Shale (Richardson, 1979; Heistand et al., 1980).

	pH	EC (mmho/cm)	Concentration (meq/100g)[a]							Concentration (ppm)[a]					
			Na	K	Ca	Mg	SO_4	Cl	HCO_3	B	P	NO_3	K	Fe	Zn
Colo. Shale #1	9.0	17.1	6.9	0.6	1.4	1.9	11.1	0.1	0.2	0.7	4.4	0.3	290	–	–
Colo. Shale #2	9.0	10.6	4.0	0.1	0.7	2.8	5.2	0.04	0.2	0.9	1.7	–	102	–	–
Colo. Shale #3	9.3	19.0	5.3	–[b]	0.5	1.8	9.0	0.04	0.1	–	5.2	0.3	460	61	13.4
Colo. Shale #4	9.0	22.0	–	–	–	–	–	–	–	0.5	3.8	0.4	480	49.2	8.4
Colo. Shale #5	10.8	9.8	3.0	–	0.7	0.1	–	–	–	1.5	–	–	–	46	0.5
Utah Shale	11.7	5.2	1.3	0.3	0.6	0.01	1.5	0.2	0.7	0.2	–	–	–	–	–

[a] Based on 1:1 extract.

[b] Not reported.

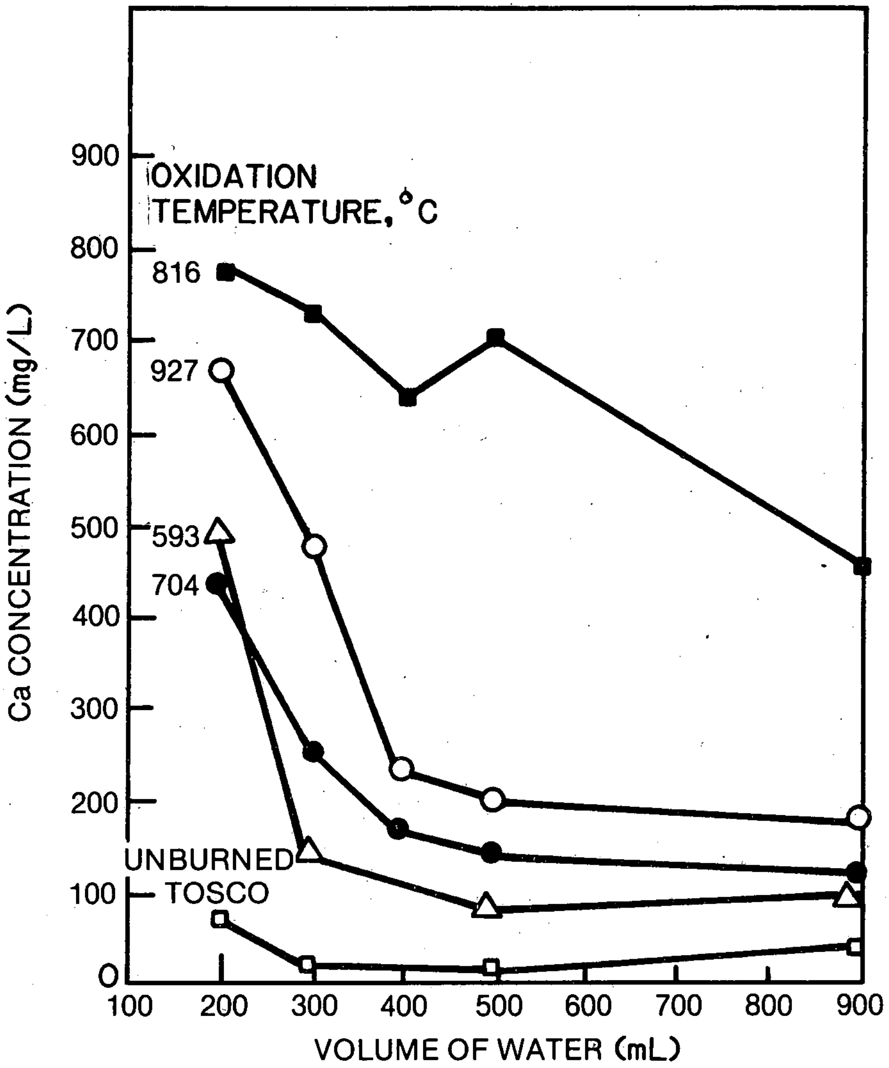

Figure 4-8. The effect of gasification temperature for a residence time of 1 hr on the Ca concentration in leachates from TOSCO spent shales. Raw shale from the Colony Mine, below the Mahogany Marker, was retorted in a TOSCO pilot plant and the resulting spent shale subjected to different char gasification conditions in laboratory reactors. The spent shales were stepwise batch leached by contacting 20 g of shale with 100 mL water for 2 to 3 days, decanting the leach solution and repeating the procedure. Thus, each successive 100 mL sample of the graph represents a single batch leach. (Modified from Culbertson et al., 1970).

In more recent work, Taylor et al. (1982) investigated the effect of char combustion temperature (350 to 800 C) on the composition of leachates. Their data are presented in Table 4-17. These investigators focused on the disposition of sulfur during oxidation and subsequent leaching, and they proposed reaction mechanisms that accounted for the observed sulfate concentrations in leachates. These equations were presented and discussed in a previous subsection on "Sulfur Reactions" in the Surface Spent Shale Mineralogy Section on page 4-16.

In general, their studies reveal that the leachability of S from spent shale depends on whether the S is present as FeS_2, FeS, $CaSO_4$, or $MgSO_4$. The sulfides are relatively insoluble while the sulfates are soluble (Table 4-3). Under pyrolysis conditions, about half of the sulfur is retained by the spent shale as FeS. At oxidation temperatures above approximately 500 C, sulfur is retained by the spent shale as sulfate, and the fraction of the sulfides converted to water soluble sulfates is proportional to the fraction of char burned. When spent shale is oxidized at 650 C and below, approximately equal amounts of $CaSO_4$ and $MgSO_4$ are formed. Oxidation at temperatures above 650 C yields mostly $CaSO_4$, and oxidation at 800 C results in complete carbonate decomposition to CaO and MgO. Table 4-17 indicates that oxidation temperature also has an important effect on the concentration of As, B, Li, Mn, and other elements in the leachates, but the underlying mechanisms were not explored in this work.

Farris (1979), in a study of cementation of surface spent shale, considered the effect of retorting temperature, time at temperature, and atmosphere on spent shale mineralogy and composition of permeate from permeability tests. His work was largely inconclusive due to the small amount of data. However, he noted that carbonate decomposition played a key role in the quality of his leachates. Mineral carbonates were observed to decompose, and carbonate leachate concentrations were 0 below 760 C and they increased sharply, to 38 to 117 ppm, above this temperature. The pH increased in direct relationship to temperature and above about 760 C, it was 11.3. He also observed that the cementing ability of his samples, reflected by compressive strength of test specimens, affected leachate quality. Some of his results for an indirect-mode sample are shown in Figure 4-9.

Codisposed Solids and Liquids

Industry plans to dispose of various solids and liquids with spent shale (Union, 1979; USDI, 1975). Some developers plan to moisturize their spent shale to cool the shale, to control dust, and to facilitate compaction. Highly contaminated wastewaters, including retort water, have been proposed for moisturization. Waste solids, including raw shale fines, catalysts, and sludges of various types, also may be codisposed with spent shale.

These liquids and solids will affect the quality of the resulting leachates. The solids may be leached, altering the composition of leachate compared to 100% spent shale. Wastewater contaminants may be retained by the spent shale during moisturization and subsequently released through leaching or volatilization as temperatures, redox conditions, microbial activity, and other variables change. Since organic matter in process waters

TABLE 4-17

Concentration (ppm) of Sulfate and Some Elements Dissolved from Retorted Oil Shale Oxidized at Various Temperatures for 30 min. The Spent Shales Were Ground to 200 Mesh and 1-5 g Was Stirred With 300 ml Distilled Water in Open Beakers for 24 hrs. (Taylor et al., 1982).

Temp. of Oxidation (°C)	SO_4	Ca	Mg	K	Na	Si	Sr	Al	As	B	Li	Mn	Mo	Pb	V	Zn
blank (unoxidized)	22	16.6	9.64	1.0	4.86	2.01	.33	0.02	0.01	0.08	0.025	0.002	0.10	0.03	0.018	0.003
350	76	27.7	15.4	1.1	7.86	1.72	.48	0.02	0.08	0.10	0.083	0.003	0.12	0.03	0.007	0.004
400	104	31.9	16.2	1.3	7.79	1.80	.59	0.02	0.09	0.10	0.097	0.002	0.16	0.03	0.007	0.004
450	128	40.7	18.7	1.4	8.22	2.24	.80	0.02	0.09	0.10	0.079	0.003	0.12	0.03	0.010	0.004
500	188	50.1	26.3	1.9	10.1	2.93	1.14	0.02	0.09	0.13	0.089	0.003	0.14	0.03	0.011	0.003
500	85	32.4	11.7	0.9	5.37	2.09	.58	0.02	0.11	0.06	0.035	0.002	0.07	0.03	0.009	0.017
500	206	53.7	28.3	2.3	9.82	3.04	1.22	0.02	0.11	0.13	0.095	0.004	0.15	0.05	0.010	0.004
550	178	44.0	27.2	2.1	7.73	3.76	1.14	0.02	0.10	0.11	0.061	0.002	0.16	0.03	0.011	0.005
600	182	31.8	38.6	3.8	9.13	3.04	1.09	0.02	0.11	0.11	0.097	0.002	0.16	0.05	0.009	0.003
600	190	39.6	27.6	4.0	9.00	3.27	1.37	0.02	0.09	0.12	0.098	0.001	0.16	0.03	0.014	0.005
650(1)[a]	45	7.67	16.3	3.4	9.62	2.19	.45	0.02	0.07	0.12	0.086	0.000	0.13	0.03	0.009	0.002
650(10)[a]	162	29.8	25.1	4.8	9.73	2.29	1.20	0.02	0.05	0.13	0.099	0.001	0.14	0.03	0.017	0.003
650(100)[a]	158	55.8	6.15	5.2	7.94	2.29	1.58	0.02	0.03	0.15	0.116	0.001	0.17	0.03	0.024	0.002
700	167	72.6	3.08	4.3	7.24	8.11	1.72	0.02	0.07	0.16	0.105	0.001	0.17	0.03	0.011	0.005
700	57	22.9	6.82	1.1	2.25	6.76	.55	0.05	0.07	0.05	0.026	0.000	0.06	0.05	0.061	0.004
780	38	15.4	.057	2.9	8.91	7.01	2.29	0.39	0.04	0.00	0.047	0.001	0.17	0.04	0.007	0.003
800[b]	66	46.5	.495	3.3	10.7	30.2	1.27	0.045	0.06	0.05	0.044	0.000	0.13	0.06	0.065	0.003
800[c]	142	17.6	5.05	22.5	45.5	13.7	0.65	0.02	0.04	0.06	0.043	0.001	0.12	0.05	0.049	0.002

[a] Duration of oxidation in min. All other samples were oxidized for 30 min.

[b] Sample mixed with water for 24 hr., exposed to air.

[c] Sample mixed with water for 72 hr., exposed to air.

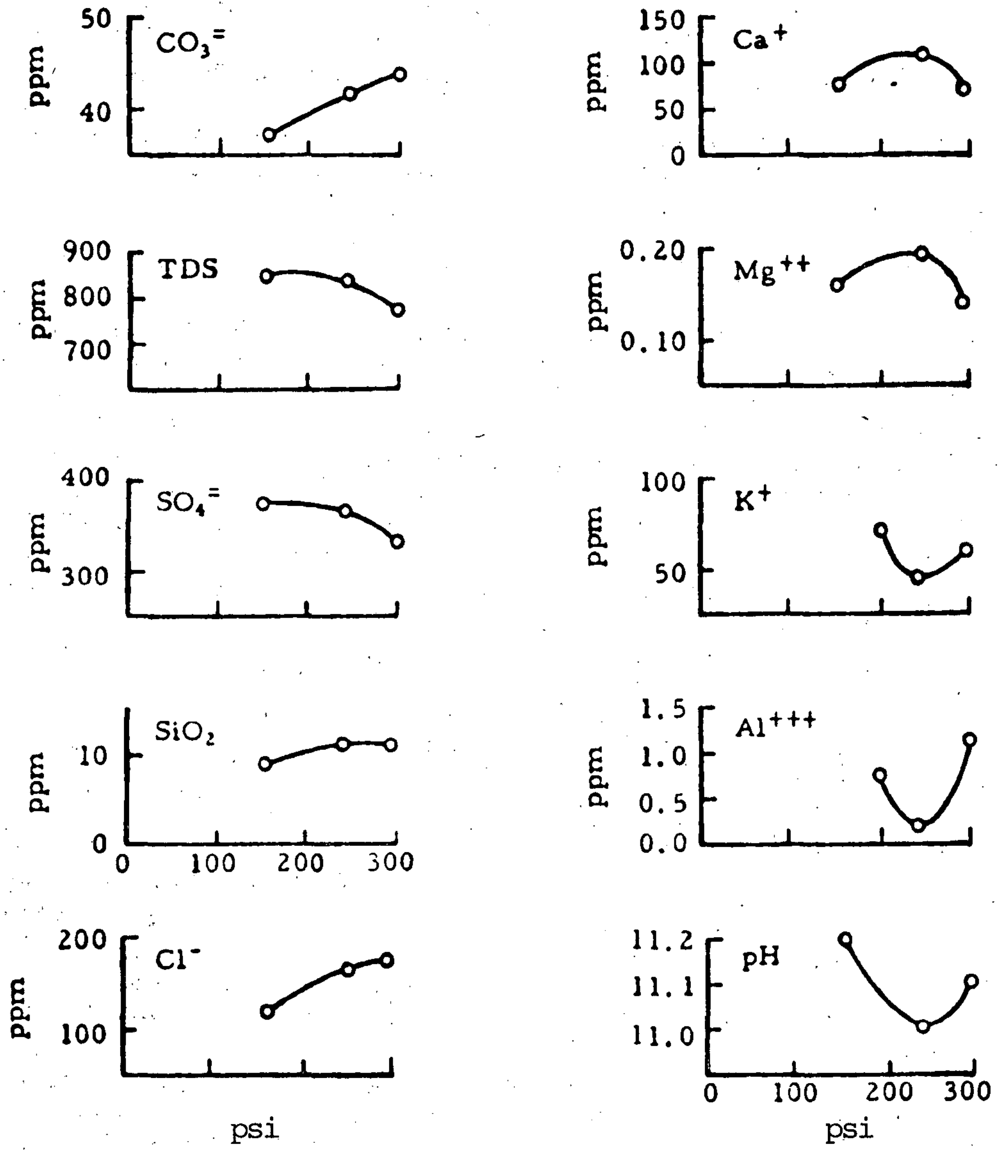

Figure 4-9. The effect of compressive strength on leachate quality of permeates from permeability tests on simulated indirect-mode spent shale (Farris, 1979).

has been shown to react with Cd, Ni, and Tl (Wildung et al., 1977), it has been suggested that organic ligands in these waters may complex metals in spent shale, increasing metal mobility (Wildung et al., 1977; Stanley et al., 1981).

The vast majority of leaching studies has not considered these effects, although there is a growing awareness of their importance (Rogers et al., 1981a; Wildung et al., 1979; Stanley et al., 1981; Fox, 1982a; Jackson and Jackson, 1982). Metcalf and Eddy (1975) and Fox (1982b) studied the effect of retort water on the organic carbon content of leachates while Farris (1971). Fox (1982a), and Jackson and Jackson (1982) considered the effect of retort water on certain major and trace elements. These studies generally demonstrate that moisturization with retort water increases some constituents and decreases others in the leachates. The underlying mechanisms are unknown and should be investigated.

Farris' results are summarized in Table 4-18. He used tap water and simulated in situ retort water to moisturize laboratory spent shale to 25% (w/w) prior to its compaction, and he leached the resulting specimens with deionized water. His leachate analyses indicate that the retort water nearly doubled the carbonate and Al concentrations in both tests and doubled the Ca content of the direct-mode sample, but had no significant effect on SO_4, SiO_2, K, Cl, or Mg. This is quite significant, considering that the retort water contained approximately 83 times as much CO_3, 16 times as much SO_4, 1350 times as much Cl, 9 times as much SiO_2, and 2.5 times as much TDS as the tap water. Mass balance calculations indicate that the spent shale retained significant amounts of the Mg, CO_3, SO_4, and Cl that was present in the moisturization water. Apparently, the ions are absorbed by the spent shale or react with minerals in the shale. Potential resolubilization of those ions should be evaluated.

In other similar work, Jackson and Jackson (1982) moisturized two samples of Paraho spent shale, a Superior spent shale, and a simulated in situ spent shale with coproduced retort waters and with distilled water, compacted the moisturized samples using ASTM D698-78, cured the resulting cores for periods of one to four weeks, fractured the cores, and batch leached the samples using the ASTM leaching test and EPA's Extraction Procedure specified in the RCRA regulations. The results of their analyses are shown in Table 4-19. This study reveals that there are important differences between various spent shales and that retort-water moisturized spent shale leachates comply with RCRA guidelines.

Mass balance calculations, using the data from Table 4-19, reveal that Paraho spent shale retains a significant amount of the As, Cl, and salts applied in the retort moisturization water even though the resulting leachate concentrations are elevated, compared to the distilled water case. This is consistent with Farris' work. Mass balance calculations also indicate that moisturization with retort water mobilizes Li, Mo, and Sr from Paraho spent shale. The Superior spent shale, on the other hand, retains only organic carbon, and moisturization enhances the mobility of As, B, Cl, EC, Li, SO_4, and Sr and has no effect on Mo or Se.

TABLE 4-18

The Effect of Moisturization Water Quality on Leachate Composition (Farris, 1979).[g]

	Moisturization Water Composition			Leachate Composition			
				Spent Shale Indirect-Mode[e]		Spent Shale Direct-Mode[f]	
	Tap Water[a]	Retort Water[a,c]	Deionized Water[b]	Tap Water[a]	Retort Water[a,c]	Tap Water[a]	Retort Water[a,c]
CO_3	180	15,000	0	37	55	37	61
SO_4	458	7,500	340	377	288	544	521
Cl	2	2,700	29	124	150	203	174
Si as SiO_2	8	74	12	9	12	9	10
Ca	62	3.7	49	76	73	119	218
Mg	<0.02	11	18	0.16	0.14	<0.05	0.07
Na	458	320	128	-	-	-	-
K	74	50	4.6	73	64	85	74
Al	81	-	<0.1	0.72	1.20	0.57	0.72

[a] Used to moisten shale before compaction.

[b] Used in leaching tests.

[c] Simulated in situ retort water from LETC's 150-ton retort.

[d] Leachates generated by crushing high-strength test cores and batch leaching 250 g in 1000 mL of deionized water.

[e] Indirect-mode samples retorted at 1,500 F for 6 hrs, and compacted samples cured 28 days.

[f] Direct-mode samples retorted at 1,600 F for 1 hr, and compacted samples cured 28 days.

[g] All values in ppm.

Neither the Farris (1979) study nor the Jackson and Jackson (1982) study is representative of conditions that will occur in a field spent shale disposal pile because they fractured their compacted cores prior to leaching. This is unfortunate since mineral phases that form in the compacted sample and which would not be available for leaching in a spent shale disposal pile, were exposed to leaching flows. Others (Fox, 1982b) have noted that these mineral reactions entrap organics and other constituents, reducing their leachability. Future codisposal work should investigate the role that self-cementing and other post-compaction mineral reactions may have on the solubility of organic and inorganic constituents in the moisturized mass.

Others have focused on the fate of organics applied in the moisturization water. Metcalf and Eddy (1975) heated TOSCO II spent shale to 180 F and sprayed it with retort water to simulate proposed moisturization procedures.

TABLE 4-19

The Effect of Coproduced Retort Waters on the Quality of Leachates From Spent Shales (Jackson and Jackson, 1982).[a]

	Moisturization Water Composition		Leachate Composition[b]			
			Paraho Spent Shale Moisturized:		Superior Spent Shale Moisturized:	
	Paraho Retort Water	Superior Retort Water	Distilled Water	Retort Water	Distilled Water	Retort Water
As	9	0.25	0.11	0.20	<0.1	0.14
B	3.6	1.83	0.19	0.15	0.16	0.29
Ba	0.15	<0.1	0.10	<0.1	<0.1	<0.1
Cl	27,500	350	59	451	>5	18
Cr	0.15	<0.1	<0.1	<0.1	<0.1	<0.1
EC (μmhos/cm)	160,000	>8,500	2,100	4,700	3,250	3,900
Li	2.9	0.18	1.1	1.4	0.51	0.63
Mn	0.17	1.23	<0.1	<0.1	<0.1	<0.1
Mo	0.47	<0.1	0.27	0.40	0.39	0.38
Ni	0.44	<0.1	<0.1	<0.1	<0.1	<0.1
Se	4.4	<0.1	0.21	0.44	0.14	0.15
SO_4	10,800	3,000	-	-	896	1073
Sr	0.75	0.21	0.20	1.4	0.33	0.39
TOC	44,000	5,000	5	1075	>20	53
pH	8.6	7.0	9.9	9.0	9.4	9.2

[a] All values in ppm except EC which is in μmho/cm.

[b] Samples produced by leaching fractured cores cured for 4 weeks using ASTM D3987 (350 g of spent shale are batch leached in 1,400 mL distilled water; the final leachate was diluted to 2,000 mL prior to analysis). Spent shale cores were produced by moisturizing each sample (Paraho - 14% water (w/w); Superior 12.5% water (w/w)) and compacting it according to ASTM D698-78.

Their work revealed that the moisturization water increased the leachate TOC by 38% compared to an unmoisturized sample, indicating that approximately 60% to 70% of the TOC in the moisturization water was absorbed by the spent shale. This is in agreement with later results by Fox et al. (1980c) who noted that TOSCO II spent shale removed 50% to 70% of the organic carbon from two samples of in-situ retort water.

Fox (1982b) investigated the fate of classes of organic compounds co-disposed with Paraho spent shales. Samples from a 1981 run of the direct-mode pilot plant were wetted with two moisture contents, 5% (w/w) and 20% (w/w) of retort water and gas condensate, compacted to field specifications (ASTM D-1557B and ½-ASTM D-698B), and extensively leached in the compaction mold under saturated conditions. The resulting leachates were collected and analyzed for dissolved organic carbon and fractionated using reverse-phase C-18 chromatography and methylene-chloride extraction at pH 13 and pH 2. A portion of the base/neutral extract also was analyzed by nitrogen-specific capillary-column gas chromatography. Some of this work is summarized in Figure 4-10.

This work demonstrated that Paraho spent shale retained a significant portion of the organic carbon applied in the moisturization water and that some compounds may be volatilized during the wetting procedures. The hydrophobic solutes are either volatilized during moisturization or are retained by the spent shale while the hydrophilic solutes are soluble and readily leached. This is clearly demonstrated in Figure 4-10. These results are consistent with other related work reported by Fox et al. (1980c) in which it was demonstrated that Paraho spent shale retained 0.44 to 0.89 mg/g of the organic carbon applied during treatment of several in situ retort waters. These results also are consistent with related work reported by Jackson and Jackson (1982) (not reported in Table 4-19) in which a sample of spent shale from the same run used by Fox (1982b) did reveal some retention of organic carbon.

In other work, Stanley et al. (1981) investigated the potential mobilization of some metals from spent shale by the formation of soluble metal-organic ligand complexes with organics in retort water. They passed Paraho, Occidental, and Omega-9 retort water and distilled water through packed columns of Paraho spent shale and analyzed the percolates for As, Se, Cd, Cr, Pb, Zn, Co, Cu, Ni, and Mo. Molybdenum was the only metal which was mobilized, and this was not believed to be due to the formation of metal complexes with retort water organics. This is consistent with increased mobility of Mo noted in Jackson and Jackson's (1982) work (Table 4-19).

Stanley et al.'s (1981) work also indicated that As was removed from retort water when passed through columns of Paraho spent shale. Initial concentrations of 5.1 mg/L As in the retort water were reduced to 0.3 mg/L in two pore volumes and sustained through 20 pore volumes. Model compound studies indicated that arsenate was completely removed while methylarsonic acid was only partially removed, suggesting that calcium arsenate may form on the spent shale. These results are generally consistent with work reported by Fox (1982a) who demonstrated that Lurgi, Paraho, and other spent shales remove arsenate from retort waters. However, Fox did not observe any removal of methylarsonic acid. No other As species were detected in the waters. The mobility of the sorbed As has not been determined and should be as this sorbed material may be released under field conditions.

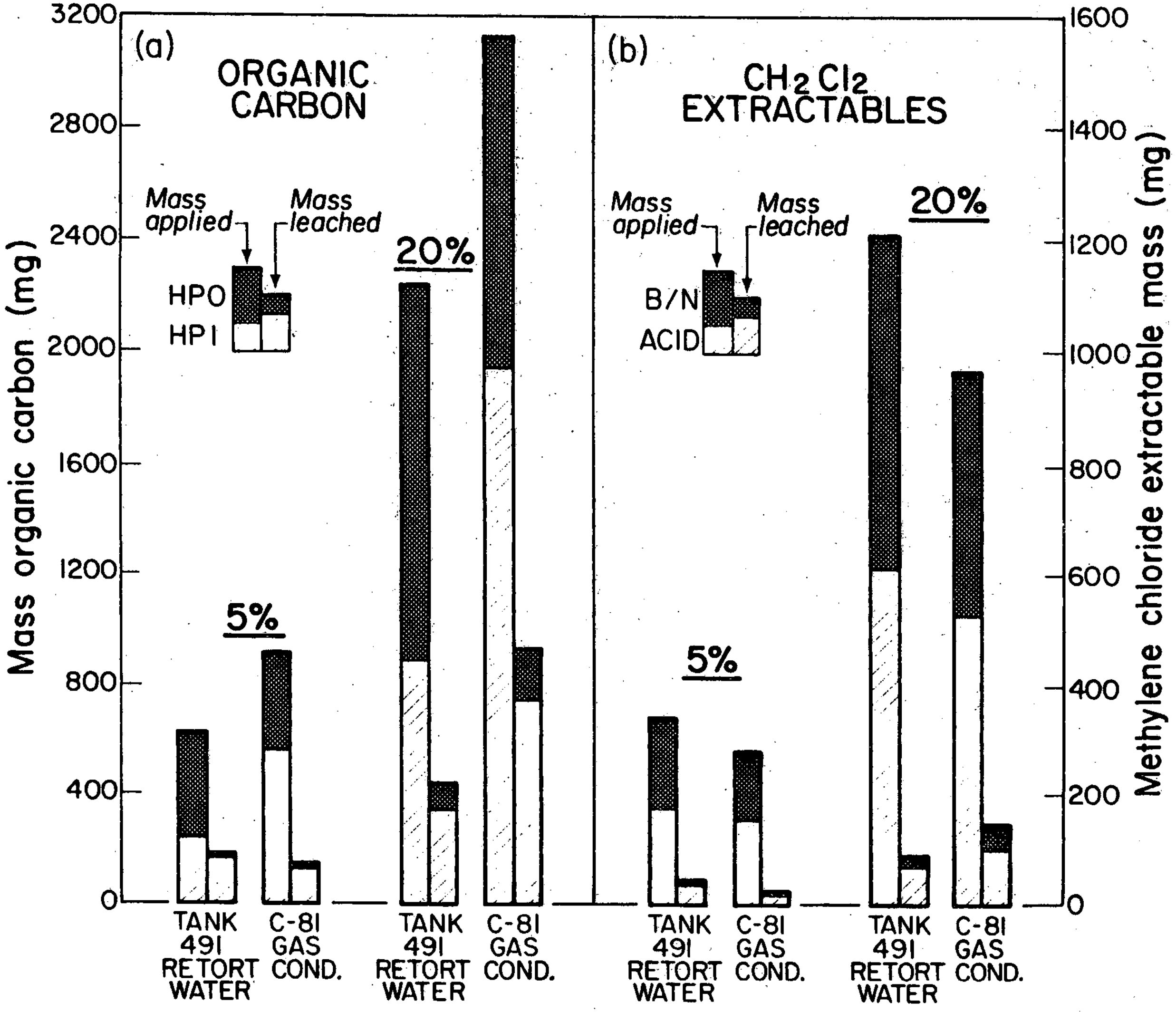

Figure 4-10. The distribution of hydrophobic and hydrophilic solutes and of acid and base/neutral methylene chloride extractables in leachates from spent shales moisturized with Paraho process waters (Fox, 1982b).

Retort and other waters used for spent shale moisturization may influence the microbial colonization of spent shale disposal piles, leading to changes in the mobility of organics and metals through alkylation reactions or by degradation of organics. Or the waters may have toxic or inhibitory properties which will affect the growth of some microorganisms important for revegetation. This is being studied at PNL by Rogers et al. (1981a). Their studies have shown that a group of organic acids, which includes benzoic acid and a series of mono- and dicarboxylic aliphatic acids, is readily degraded in the early stages of growth of a mixed population of soil bacteria using Paraho retort water as the sole source of carbon and energy (Rogers et al., 1981a). Their results suggest that 30% or more of the organic compounds in retort water used for spent shale compaction may be readily degraded under aerobic conditions, assuming conditions appropriate for microbial growth. This could decrease the concentration of soluble organic carbon in field leachates, compared to results predicted from laboratory studies (Metcalf and Eddy, 1975).

The only study on the effect of codisposed solids on leachate quality was reported by Union (1979c). They analyzed a single sample consisting of 90% Union B spent shale and 10% raw shale fines (the mix they proposed to dispose of) for TDS, F, and B. The latter two elements were chosen because these are the only elevated trace elements in Union B leachates (Table 4-10). There was no difference between the composition of this mixed sample and another sample of 100% retorted shale. Studies of other solids, especially catalysts and other potentially hazardous substances, are required.

Pile Design

Various aspects of pile design, including compaction, face slope, erosion control measures (rip-rap), and others will affect the quality and quantity of runoff and percolation. Compactive effort, in particular, has an important effect on leachate quality and has been studied experimentally.

Compactive effort may affect leachate composition by altering the internal porosity and/or the surface properties of the disposal pile. Thus, compaction affects the liquid-to-solid ratio, which ultimately controls leachate composition. This is discussed in the section "Physical, Chemical, and Biological Processes" on page 4-77. Compactive effort and the related properties, permeability and bulk density, are discussed here. The reader also is referred to page 4-79 for a discussion of the underlying mechanisms. Slope was considered previously in the model studies section.

Many studies have demonstrated that the permeability of spent shale can be reduced to low levels through proper compaction (Holtz, 1976; Farris, 1979). This is demonstrated by the permeability test results for four separate spent shales in Table 4-20. Because each spent shale is unique, compactive effort, dry density, and permeability will differ in individual disposal designs. Thus, these should be considered in laboratory and lysimeter studies.

This permeability decrease is due to a reduction in particle size of the sample during compaction and subsequent plugging of voids with the fine material and to natural cementation reactions that occur in the moisturized spent shale (Holtz, 1976; Culbertson et al., 1970). Interlocking crystals of calcium aluminum silicate are formed at the points of contact between spent shale fragments which reduce the permeability and increase the strength of the material (Farris, 1979). The formation and presence of this new mineral phase will affect the leaching characteristics of the spent shale. This phase apparently is not important in uncompacted columns and batch tests.

TABLE 4-20
The Effect of Compactive Effort on Spent Shale Permeabilities (Holtz, 1981).

	Compactive Effort	Permeability (ft/yr) Under Loadings of:		
		50 psi	100 psi	200 psi
Coarse shale High temperature	Light	15.0	5.5	1.7
	Standard	7.0	1.4	0.8
	Heavy	1.1	0.6	0.1
Fine shale Low temperature	Light	-	0.4	0.3
	Standard	-	0.4	0.4
	Heavy	-	0.4	0.2
Fine shale Very high temperature	Light	0.003	0.003	0.002
	Standard	0.002	0.005	0.001
	Heavy	0.001	0.001	0.001
Coarse shale Low temperature	Light	114.6	40.4	18.9
	Standard	54.0	44.5	26.4
	Heavy	9.1	7.1	6.4

The work of Holtz (1976) demonstrated that compactive effort can have an important effect on leachate quality. He studied the effect of low (44 psi), medium (86 psi), and high (390 psi) compactive efforts on the composition of permeates from permeability tests. Some of his results for Paraho direct-mode spent shale are presented in Table 4-21 and compared to a standard leach test (0.1 g/mL for 6 hrs) which is similar to that used by many leachate researchers. These data indicate that there are some important differences between the quality of leachate produced by the standard test (uncompacted) and the compacted test materials. In particular, the concentrations of TDS, Na, and K are much higher in leachates from compacted samples than from the uncompacted samples. The concentrations of these three constituents also increase with compactive effort for most experimental conditions. Other constituents, including pH, Si, Fe, Mg, SO_4, and HCO_3, show no discernible trends with respect to compactive effort. However, SO_4 and HCO_3 are much higher in compacted samples for most experimental condition.

The effect of compaction on surface properties is also important. In lysimeter studies on TOSCO II spent shale, Ward and Reinecke (1972) and Margheim (1975) observed that the concentration of dissolved ions in runoff is directly related to surface bulk density (ρ) and inversely related to permeability (k) or $C \propto (\rho/k)$. Thus, increased compaction reduces the quality of runoff. The reason for this increase in concentration is uncertain, and it may be due to particle degradation and an attendant increase in surface area. Since spent shale probably will be covered by a soil layer, this relationship may not be important in understanding water movement in a commercial spent shale pile.

In other work, Malek (1981) explored the effect of compaction on the EC of Paraho column percolates. Using three water application rates, he found that compaction did not significantly affect the EC of his percolates.

These studies generally indicate that the degree of compaction can influence certain constituents in runoff and percolates. Laboratory samples usually are not compacted. This could contribute to differences between laboratory and lysimeter studies.

TABLE 4-21

The Effect of Compactive Effort on the Quality of Percolates From permeability Tests of Paraho Direct-Mode Spent Shale (Holtz, 1976).

Compactive Effort[b]	Permeability Rate (Ft/Yr)	Effluent taken at: (Days)	pH[a]	TDS (ppt)	Si (ppm)	Al (ppm)	Fe (ppm)	Ca (ppm)	Mg (ppm)	Na (ppt)	K (ppm)	Li (ppm)	SO_4 (ppt)	CO_3 (ppm)	HCO_3 (ppm)	Cl (ppm)
(Standard Leach)[c]			11.1	1.4	8	1.3	0.1	200	9	0.2	50	-	0.5	180	<0.1	69
Low	30	1	7.5	6.9	5	<0.1	0.1	408	47	1.3	289	-	3.3	<0.1	230	580
	15	5	11.4	2.4	5	0.3	<0.1	250	8	0.5	74	-	0.3	700	<0.1	68
	7.5	10	9.0	5.6	9	<0.2	1.1	18	15	1.4	237	-	2.9	90	290	71
	2.3	20	8.9	4.4	6	1.4	0.8	13	1	1.1	171	17	6.9	98	550	120
Medium	22	1	8.0	7.2	3.7	0.2	0.8	243	7	1.8	312	-	3.1	72	180	670
	7.5	5	11.4	3.3	5	<0.1	0.1	164	5	0.8	252	-	0.8	410	<0.1	230
	2.2	10	9.6	5.6	15	<0.2	1.0	6	2	1.5	245	-	2.6	310	280	36
	0.8	20	8.4	3.7	8	1.6	1.1	6	3	0.8	304	2	1.4	45	710	31
High	3.2	1	7.8	9.2	9	<0.1	0.3	157	37	2.1	445	-	4.3	<0.1	330	790
	1.0	5	7.4	8.2	9	<0.1	0.1	157	42	1.9	334	-	4.0	<0.1	320	580
	0.4	10	9.0	11.6	9	<0.2	0.4	16	10	2.9	304	70	6.3	96	630	71
	0.1	20	7.8	6.8	7	0.8	2.2	57	12	1.6	312	10	3.7	<0.1	300	62

[a] All data except pH in parts per million (ppm) or parts per thousand (ppt).

[b] Compactive effort: low, 6200 ft-lb/cu ft.; medium, 12,375 ft-lb/cu ft.; high 56,200 ft-lb/cu ft.

[c] Water:shale ratio was 10:1 (wt:wt); tumbled 6 hours at room temperature.

Reclamation Procedures

Vegetation will be established on spent shale disposal piles for aesthetic and environmental reasons. Research, reviewed by Redente et al. (1980) and Redente and Doerr (1981), indicates that three approaches to reclamation are being considered: (1) establishment of salt-tolerant or adapted vegetation directly on spent shale, (2) modification of spent shale to improve its suitability for plant growth prior to vegetation, and (3) covering the spent shale with soil or other geologic material prior to vegetation. These various types of treatments will affect the volume and quality of runoff and percolation from disposal piles.

The effect of several important aspects of reclamation (water application rate, soil cover depth, preleaching) is being studied in lysimeters by CSU. They have investigated TOSCO II (Harbert and Berg, 1978; Kilkelly et al., 1981a,b), Paraho (Harbert et al., 1979; Kilkelly et al., 1981c), and Union SGR (Herron et al., 1980) spent shales at two separate sites that are representative of the different climatic conditions in oil shale regions. They are monitoring EC, sediment, and pH in runoff and percolation; some samples are analyzed for major ions. Battelle also is measuring a range of major, minor, and trace elements (Table 4-9) in the percolate from the high-elevation Paraho lysimeter (Garland et al., 1979). In other work, Malek (1981) studied the effect of four different soil stabilizing materials on the volume and quality (EC, sediment, pH) of runoff and percolation. Some of the more significant results relevant to leachate composition and water movement are summarized for each spent shale.

TOSCO II. The effect of preleaching and soil cover depth on the quality of runoff was studied in lysimeters at a high (2200 m) and a low (1700 m) elevation site in Colorado (Harbert and Berg, 1979; Kilkelly et al., 1981a). Some typical results from these studies are summarized in Table 4-22. In general, soil cover reduced the concentration of Na, Ca, Mg, K, HCO_3, and SO_4 and had no effect on Cl or pH in runoff waters. The concentration of most dissolved ions in runoff from the 30-cm cover tended to be slightly lower than for the 15-cm cover and similar to a soil control (not shown in Table 4-22). This is probably because salts did not migrate through the entire 30-cm layer and accumulate at the surface where they could be solubilized. Application of sufficient preleaching water controlled the accumulation of these salts at the surface, slightly improving the quality of runoff.

These CSU lysimeter studies also indicated that no percolation occurred at the two sites, even though the shale was not compacted (some light compaction occurred at the high elevation site). At the low-elevation site, moisture recharged to a depth of 90 to 140 cm for all spent shale treatments as a result of normal to above-normal precipitation in 1974 - 1976 (mean is 30 cm). Similar trends were noted in continued monitoring during 1977 - 1980 (Kilkelly et al., 1981a). At a higher elevation site located along Black Sulphur Creek (2200 m), moisture penetrated only to a depth of 30 cm and most of the 150 cm

TABLE 4-22

The Effect of Surface Treatment and Aspect on the Quality of Snowmelt Runoff from Lysimeters of TOSCO II Spent Shale, March 13, 1975, Piceance Basin (Harbert and Berg, 1978).

	North Aspect			South Aspect		
	Leached TOSCO II (ppm)	Leached TOSCO II +15 cm Soil Cover (ppm)	Unleached TOSCO II +30 cm Soil Cover (ppm)	Leached TOSCO II (ppm)	Leached TOSCO II +15 cm Soil Cover (ppm)	Unleached TOSCO II +30 cm Soil Cover (ppm)
pH, units	7.4	7.5	7.4	7.8	7.8	7.7
EC, μmho/cm	725	240	135	375	160	95
Na	12	7	5	2	7	2
Ca	90	25	16	63	18	11
Mg	23	8	4	4	4	1
K	20	6	4	4	4	2
HCO_3	91	88	73	61	73	34
SO_4	307	38	7	160	10	6
Cl	7	7	4	4	4	4

of applied water (for leaching) was evaporated. During the 1977 - 1980 season (Kilkelly et al., 1981a), spring snowmelt resulted in moisture penetration to depth of 60 to 120 cm. The Metcalf and Eddy (1975) study also found that it was difficult to get moisture to move through their lysimeter of TOSCO II spent shale, and they used high water application rates, 0.79 in/hr for 8 hr/day (equal to the average annual rainfall at Davis Gulch), to generate adequate volumes of percolation for study. Another study at the Colony embankment (Heley, 1976) revealed that little or no moisture movement occurred below a few feet in four years of field weathering.

These results indicate that water will move through the pile if continuously applied. When application ends, capillary forces move the moisture to drier regions, such as the surface of the pile, where it is rapidly evaporated. Additional, long-term testing is required to assure that repeated water applications do not slowly drive the moisture front deeper into the pile.

Paraho Direct-Mode. Similar studies are being conducted with Paraho spent shales (Harbert et al., 1979; Kilkelly et al., 1981c). The variables they have studied and some of their results are summarized in Table 4-23. Four years of study at these sites indicates that percolate EC fluctuates widely but that an overall decrease with time occurs. The largest ECs and greatest volume of percolate were usually associated with spent shale plots that had

TABLE 4-23

Summary of Percolation Data From CSU Lysimeter Studies of Paraho Spent Shale for 1978 (Kilkelly et al., 1981c).

Treatment	Slope	Total Yearly Percolate (liters)	EC Max (mmhos/cm)	EC Min (mmhos/cm)	pH Max	pH Min
High Elevation						
Paraho Spent Shale[a]	2%	903.1	11.6	7.4	9.1	7.7
	25%	7,171.8	16.6	6.2	9.1	7.7
20 cm Soil/Paraho[a]	2%	223.7	11.7	7.3	9.3	7.3
	25%	5,969.3	15.4	10.1	9.4	7.8
40 cm Soil/Paraho[b]	2%	817.6	16.2	14.4	9.8	9.7
	25%	5,059.0	29.7	20.5	9.2	8.4
60 cm Soil/Paraho[b]	2%	0	0	0	0	0
	25%	2,487.9	22.3	9.3	9.1	7.9
80 cm Soil/Paraho[b]	2%	199.1	21.0	11.2	8.9	7.3
	25%	3,384.2	31.6	21.9	8.8	8.4
Soil Control[b]	2%	12.0	3.3	2.3	8.6	8.4
	25%	4.0	2.9	2.4	8.8	8.6
Low Elevation						
Paraho Spent Shale[a]	2%	15.0	13.0	8.8	8.3	8.1
	25%	0	0	0	0	0
20 cm Soil/Paraho[a]	2%	5.0	12.6	0	8.3	0
	25%	60.0	20.0	0	8.0	0
40 cm Soil/Paraho[b]	2%	0	0	0	0	0
	25%	0	0	0	0	0
60 cm Soil/Paraho[b]	2%	0	0	0	0	0
	25%	0	0	0	0	0
80 cm Soil/Paraho[b]	2%	0	0	0	0	0
	25%	0	0	0	0	0
Soil Control	2%	0	0	0	0	0
	25%	0	0	0	0	0

[a] Leached

[b] Unleached

been leached and irrigated to establish vegetation. The effect of these variables on other constituents is being studied (Wildung et al., 1978 - 1981). However, the results of their studies are not available yet. Preliminary results (Wildung et al., 1978) suggest that 20 cm of soil cover does not significantly affect the organic carbon concentration of percolate compared to a sample with no soil cover (both were leached).

The water movement pattern in these lysimeters is less conclusive than in TOSCO II equivalents. Water moved rapidly through retorted shale and soil control treatments on high-elevation lysimeters (Harbert et al., 1979). On the low-elevation lysimeter, preleached treatments (bare spent shale and 20-cm soil/spent shale) produced percolation while moisture did not move below 105 cm for unleached treatments. The results from these studies indicate that it may be feasible to design a soil layer to retard the downward movement of moisture.

Union SGR. Other studies of Union SGR spent shale located in lysimeters near Union's Long Ridge site (elevation 2300 m) evaluated the effect of a 15-cm soil cover on the EC, pH, and sediment content of runoff and percolation. The runoff results are summarized in Table 4-24. No percolation was observed in the soil-covered lysimeter in any season, and thus, its effect on percolate quality cannot be assessed. These studies indicated that runoff volume from soil-covered shale was greater than from bare shale. The runoff EC was considerably lower during all seasons and for all water applications for the 15-cm soil cover. Sediment yields were frequently higher from the soil-covered plot.

TABLE 4-24

The Effect of a 15-cm Soil Cover on Runoff Quality From Preleached Union SGR Spent Shale (Herron et al., 1980).

	1975 Spring	1975 Irrigation	1976 Spring	1976 Summer	1977 Spring	1977 Summer	1978 Spring
	------Leached Union SGR Spent Shale with 15-cm Soil Cover--------						
Total runoff, cm	1.4+	0.8	6.5[a,b]	0.7	3.5	1.6	7.3
Electrical Conductivity, μmhos/cm	62[b]	663	100	248	120	160	43
Sediment Yield, kg/ha	-	-	3	1,684	1	1,240	134
	--------------Leached Union SGR Spent Shale---------------------						
Total runoff, cm	0.6	0.2	1.5[a,b]	0.1	1.5	0.1	1.1
Electrical Conductivity, μmhos/cm	224[b]	880	290	260	604	215	230
Sediment Yield, kg/ha	-	-	29	33	35	24	10

[a] The collectors on these treatments were found to leak in 1976; thus, this value is low.

[b] Estimated from total dissolved solids.

Climate

This is probably the most important primary variable that affects leachate production. Variables such as ambient temperature and rainfall intensity and timing will affect the degree to which natural cycles of freezing and thawing, wetting and drying, and rainfall and snowmelt alter leachate quality and volume.

In the oil shale region of western Colorado, evapotranspiration exceeds precipitation, and flash floods are common. Precipitation ranges from 10 to 12 inches per year in the deep valleys bordering oil shale outcrops near Rifle to 20 to 30 inches, most of which falls as snow, on the high plateau on top of the Green River Formation. At these high elevation sites, particularly those with north aspects, annual precipitation may exceed plant growth requirements during the spring snowmelt period.

These types of variables and conditions influence the quantity and quality of leachates and have been studied in lysimeters (Harbert and Berg, 1978; Harbert et al., 1979; Kilkelly et al., 1981; Herron et al., 1980; Ward and Reinecke, 1972; Margheim, 1975) and in the laboratory (Fransway, 1980; Stollenwerk, 1980). The lysimeter studies have produced a wealth of information. However, the majority of these data has not been rigorously analyzed as the focus of that work was on vegetative stabilization rather than leaching (Harbert and Berg, 1978; Harbert et al., 1979; Kilkelly et al., 1981; Herron et al., 1980). The detailed information, reported in the appendices of those reports should be reduced and used to develop, modify, or verify overland flow and percolation models. Others have used lysimeter results to develop models of the runoff (Ward and Reinecke, 1972; Ward et al, 1971; Margheim, 1975) and percolation (Margheim, 1975) processes. These were discussed previously. This information will be used here to present a qualitative description of the interaction of climatic variables with spent shale piles. The reader is referred to the original manuscripts for more detailed information.

The first waters that appear as runoff during a precipitation event carry the highest concentration of dissolved solids. These concentrations decay rapidly to low levels (Figure 4-11). The magnitude of this initial peak largely depends on the volume of water, the mass of salts present on the surface, and the time since the last runoff. The quantity of salts present on the surface depends on the amount of water that percolates into the pile and the amount of subsequent evaporation. Since cold winter weather postpones the drying of the shale, the greatest quantity of salts usually appears on the surface in the late spring, after the shale has had time to dry to a considerable depth. Thus, the first summer rainfall produces the poorest quality runoff. The quantity and quality of spring snowmelt, on the other hand, apparently depends on whether the ground surface is frozen or thawed.

Relatively less is known about the formation, volume of, and composition of percolation from a field spent shale disposal pile, and this issue remains highly controversial. Broadly, water that infiltrates the pile subsequently may move upward under the influence of capillary forces and evapotranspiration or downward. The record is not conclusive regarding the movement of moisture within a spent shale disposal pile, and additional study is required to determine the conditions under which such movement may be expected.

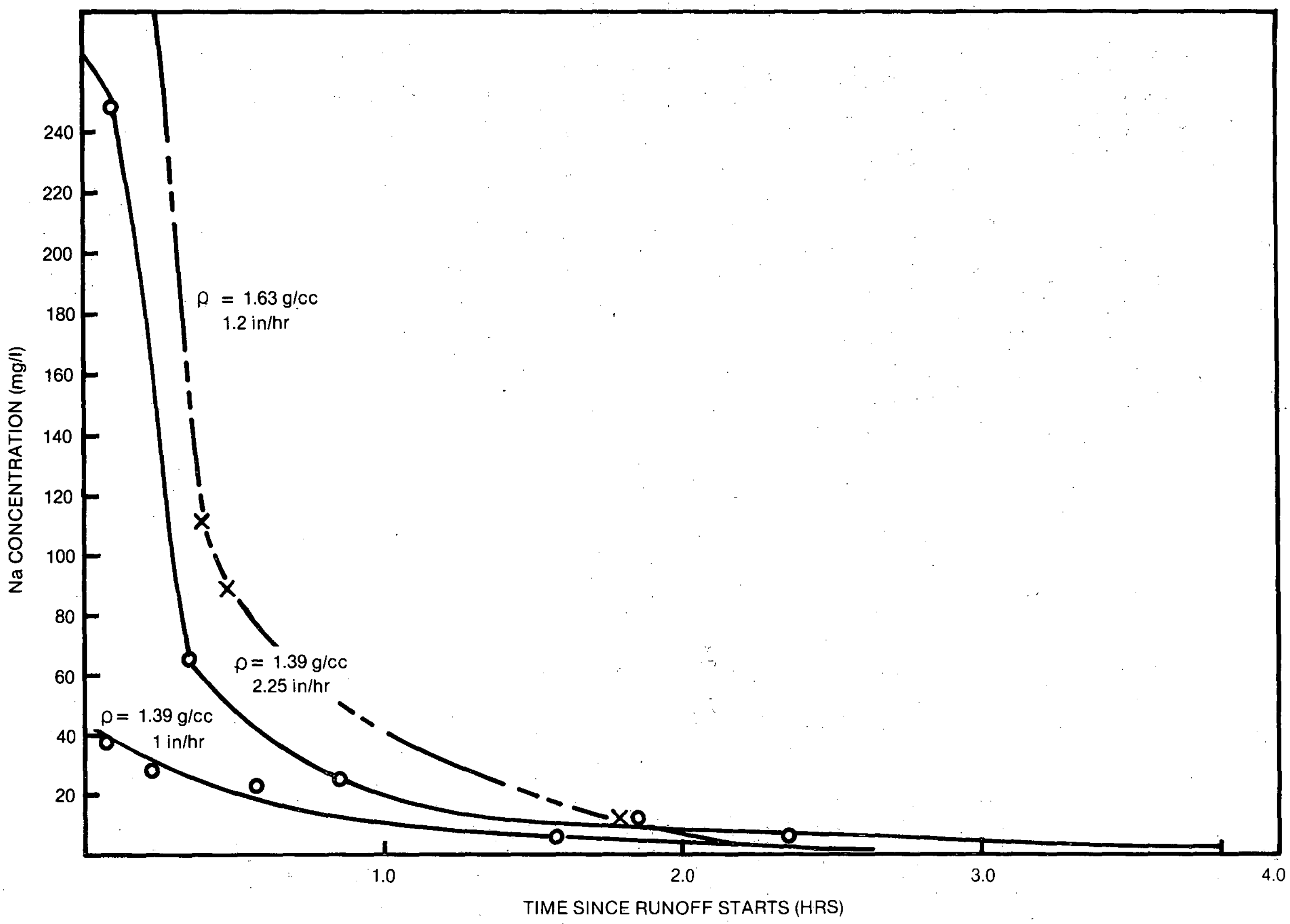

Figure 4-11. The effect of rainfall intensity and spent shale bulk density on the concentration of Na in runoff from field lysimeters filled with TOSCO II spent shale (Margheim, 1975).

The quality of percolation follows the general trends observed in laboratory columns. Initial percolates have the highest concentration of dissolved solids; concentrations drop off after this initial pulse.

Successive periods of wetting and drying will be important in spent shale disposal schemes. Some reclamation plans call for leaching soluble salts from spent shale prior to vegetation by wetting and drying the material several times (Harbert et al., 1979). Additionally, the near-surface environment of spent shale piles will be subject to periods of wetting and drying due to the unique climatic conditions existing in the oil shale region. Repeated infiltration of rainfall and snowmelt followed by evaporation will likely occur. The length of time the shale remains wet and the number of wet-dry cycles will influence leachate quality. Stollenwerk (1980) has studied both variables. In his study of wet-dry cycles, he successively saturated spent shales and dried them under a heat lamp. After this procedure had been repeated the requisite number of times, he leached the resulting samples. The effect on leachate quality of this treatment generally depended on the specific spent shale (Paraho or two samples of TOSCO II material). This treatment dramatically increased the Se concentration and had no effect on F concentration of all leachates. For the Paraho sample, it decreased pH and As, increased TDS and Mo, and had no effect on B. The results for the two TOSCO II samples were variable. No effect was noted on TDS, B decreased, and results for other parameters were inconclusive. These studies suggest that long periods of wetting and drying will alter the leachate quality, compared to that observed during early periods of weathering, or in laboratory studies.

In the contact time studies, Stollenwerk (1980) saturated columns packed with the same three shales for periods of 0.3 to 18 months prior to leaching. He then leached the equilibrated columns and analyzed the first pore volume in thirds for TDS, pH, Mo B, F, As, and Se. There was no change in Mo concentration for any of the samples. For Paraho leachates, the pH increased, there was a small increase in TDS and Se, and no effect on the concentration of Mo, B, F, or As for increasing equilibration times. For TOSCO leachates, large increases in B and F occurred for both samples, and there was no change in pH for either. These results suggest the percolates and runoff from the first spring snowmelt may have different compositions than those produced at other times due to longer winter contact times between shale and water.

Physical, Chemical, and Biological Processes

The quality of leachates is governed by various "release" and "transport" mechanisms. Dissolved substances may be "released" from the rock matrix by various physical (desorption), chemical (dissolution, oxidation), and biological (degradation, alkylation) processes. These materials are "transported" away from their release site, and their form and concentration are modified by other physical (adsorption, ion exchange, diffusion, dispersion), chemical (precipitation, reduction), and biological (degradation) reactions that occur between spent shale, dissolved material, and microbes present in the pile.

A qualitative understanding and kinetic and thermodynamic data for these mechanisms are required to understand and model the leaching of surface spent shale piles. These types of mechanisms are being probed in the laboratory by studying the effect of shale particle size, liquid-to-solid ratio, equilibration time, and microbial activity on various aspects of leachate quality. For example, information on the effect of particle size and liquid-to-solid ratio can help determine whether mineral solubility or simple desorption control the release of materials from spent shale. If solubility is controlling, the amount of material released should be independent of particle size and liquid-to-solid ratio. However, if desorption is controlling, the amount of material leached should increase as some function of particle diameter and liquid-to-solid ratio.

This section will focus on physical, chemical, and biological processes that occur in the immediate vicinity of a particle of spent shale. The effect on leachate composition of liquid-to-solid ratio, particle size, contact time, and biological activity will be investigated because these are the only aspects that have been studied. The majority of this work has focused on B and F which are elevated in leachates from all spent shales studied to date. Other work has considered As, Se, Mo, pH, and dissolved salts. Laboratory and analytical studies are also underway at PNL to develop a geochemical model of the leaching process (Wildung et al., 1977-1981).

Physical and Chemical Processes. The concentrations of ions in solution is affected by one or more of the following: solubility of a mineral phase in the spent shale (primary solubility); solubility of a mineral phase formed by precipitation from aqueous solution (secondary solubility); adsorption/desorption interactions between the spent shale and the leaching solution; and ion exchange equilibria. Identifying the specific reaction(s) which occur for any given ion or group of ions is a complex chemical problem which requires study of physico-chemical associations of the ion in the spent shale and the concentration and chemical form of the ion in the leachate.

Very little comprehensive work along these lines has been conducted on oil shale leachates. Several investigators have probed the mechanisms responsible for noted leachate composition by varying the particle size, liquid-to-solid ratio (R), equilibration time, and others. Unfortunately, the majority of this work has not been coupled with investigations of the mineral residence of the subject element nor with studies to speciate the element in the leachates and, thus, the results are largely inconclusive.

Runnells and his students at the University of Colorado (Stollenwerk, 1980; Saether, 1980; Saether and Runnells, 1977-1981; Glaze, 1981; Runnells and Esmaili, 1981; Runnells et al., 1979, etc.) have employed a variety of physical and chemical techniques to unravel the aqueous chemistry of spent shale leachates. Their work has revealed that the release of B and F from Paraho and other spent shales is controlled by desorption. Considerable additional work along these lines is required to develop a fundamental understanding of the aqueous chemistry of certain environmentally important trace elements, including Li, V, Mo and S forms in spent shale leachates.

The pertinent experimental work that has been directed at understanding leaching mechanisms is reviewed here. This work has used changes in leaching variables [i.e., liquid-to-solid ratio (R) and particle size] to infer underlying mechanisms. The analytical framework used to interpret these studies is broadly outlined here.

The release of an element from a solid in contact with water may follow one of two principal mechanisms. The first type includes desorption or ion exchange from surface sites. Because the number of surface sites exposed to the liquid increases with the amount of solid present, the concentration of the element in solution increases with decreasing R and particle size (larger surface area per unit mass of material). The second type of release mechanism occurs when an element is dissolved from a mineral phase. If there is enough solid to saturate the solution and to remain present in excess, the concentration of the element in solution should be dependent on the solubility of the mineral and independent of R and particle size. Deviations from this behavior are expected due to complexing of the element in solution and if the mineral has an ion common with some other solid phase.

Several investigators (Fransway, 1980; Silviera et al., 1978; Glaze, 1981; Glaze and Runnells, 1980) have used this approach to determine the mechanisms responsible for the release of major ions and some trace elements from Paraho spent shale. Fransway studied as-received and sieved fractions in the -2 mm and -1 mm size range. His results for the sieved fractions are presented in Table 4-25. (Note the large excess of Mg over Ca which is unusual for Paraho leachates and which suggests that Mg was present as $MgSO_4$.) The concentration data in that table reveal two trends. First, for high values of R (50 - 1000 mL/g), the concentrations of major ions are independent of particle size in the -2 mm to -1 mm size range. This suggests that for relatively dilute solutions, leachate concentrations of EC, Ca, Mg, Na, K, Cl, and SO_4 are controlled by the solubility of a mineral phase. For lower values of R (1 - 10 mL/g), the significance of differences in concentrations among the two particle sizes is uncertain and inconclusive. Analytical accuracy was not reported, and most measurements are close, within 10% of one another, for the same R.

The second trend apparent in Fransway's data is that the concentration of all of the elements studied decreases with increasing R for both particle sizes. This behavior could be due either to dissolution of a solid mineral or to a surface reaction. Additional insights were gained into the behavior of Fransway's samples by calculating the quantity of material extracted per gram of shale leached (unit mass leached). We found that the unit mass leached was independent of R for R = 1 - 10 mL/g for Cl, SO_4, K, Ca, and Mg, suggesting that these elements are controlled by a secondary solubility reaction, i.e., these ions are precipitated from solution by some other unspecified ion(s). Carbonate may control the concentration of Ca while OH may control the concentration of Mg. An inflection point occurs in the unit mass leached for R = 50 mL/g for all ions studied. This suggests that one or more ions were released into solution which removed existing secondary solubility controls. For values of R greater than 10, the unit mass of SO_4 and Mg leached is again independent of R though higher than for $R < 50$. Potassium, Ca, and Na increase as a function of R for $R > 50$, suggesting that solubility of a spent shale mineral is controlling. This is consistent with the analysis of the particle size data.

In other work, Silviera et al. (1978) studied sieved fractions of Paraho spent shale over the range of -0.15 mm to -0.63 mm using batch tests (10 mL/g; t = 3 days). Increased effective maximum particle size resulted in increases in Na, decreases in EC, Cs, Mg, and Sr, and little change in pH or K concentration. These results cannot be readily compared with those of Fransway (1980) because the range of variables each studied does not overlap.

TABLE 4-25

The Effect of Particle Size and Liquid-to-Solid Ratio on Major Ions in Paraho Direct-mode Leachates Generated in Batch Test for t = 24 hrs. (Fransway, 1980).

Particle Size: -2mm

Liquid-to-Solid Ratio (mL/g)	EC (μmhos/cm)	Concentration (mg/L)					
		Ca	Mg	Na	K	Cl	SO_4
1	16.45	20.4	141.8	93.1	9.6	1.4	315.5
2	8.0	12.5	52.8	35.8	4.3	1.2	120.3
5	5.2	7.0	29.7	51.3	2.6	0.7	70.7
10	3.1	1.8	4.7	3.8	0.5	0.4	9.4
50	0.86	2.0	4.1	2.2	0.3	0.3	8.4
100	0.46	1.2	1.9	0.9	0.2	0.2	3.8
500	0.12	0.4	0.4	0.3	0.05	0.2	0.7
1000	0.08	0.3	0.2	0.2	0.03	0.1	0.4

Particle Size: -1mm

Liquid-to-Solid Ratio (mL/g)	EC (μmhos/cm)	Concentration (mg/L)					
		Ca	Mg	Na	K	Cl	SO_4
1	15.35	21.9	124.2	156	13.4	2.6	289
2	7.6	12.5	52.2	52.2	5.3	1.2	121.3
5	3.4	4.4	16.8	27.4	1.6	0.6	38.3
10	1.8	2.8	9.8	8.3	0.8	0.4	19.5
50	0.81	2.1	3.9	2.2	0.3	0.4	7.5
100	0.46	1.3	1.9	0.9	0.2	0.2	3.8
500	0.12	0.4	0.4	0.2	0.04	0.2	0.7
1000	0.08	0.3	0.2	0.2	0.03	0.1	0.4

Glaze (1981) also studied the effect of particle size of Paraho spent shale (in the size range of -2 mm to 5 mm) on leachate composition using batch tests (5 mL/g; t = 70 hrs). No difference in the pH or B and F concentration was observed in these leachates, suggesting that a solubility mechanism was controlling.

In other more extensive work, Saether (1980) and Glaze (1981) used R and equilibration time studies to determine that the release of both B and F from Paraho spent shale is controlled by a desorption mechanism. Silviera et al. (1978), in similar work, found that the leachate concentration of Ca, Sr, and Mg decreased as R increased and that R had no effect on Na and K. The results for Ca, Sr, and Mg are compatible with either dissolution or desorption, while the results for Na and K are compatible with a solubility phenomenon.

Saether (1980) conducted additional studies on the mechanisms of release and uptake of F in Paraho leachates. He found that F is released within less than six hours after contact with water. The release mechanism follows a Langmuir-type equation, with a negative partition coefficient. The major control on the solubility of F in leachates is the abundance of dissolved Ca, and the precipitation of fluorite, CaF_2, limits F solubility. In other work, Saether et al. (1981) demonstrated that F is associated with illite in Mahogany Zone raw shales, which is consistent with desorption as a release mechanism.

Column experiments also provide information on leachate composition and release and transport mechanisms, and they are often used to develop kinetic and mass transfer data to model the leaching process (Amy, 1978; Hall, 1982). A large number of column studies have been conducted using surface spent shales but most of these have been exploratory in nature, seeking to identify leaching "trends" and to determine leachate composition (Schmehl and McCaslin, 1973; Ward et al., 1971; Margheim, 1975; Silviera et al., 1978; Stollenwerk, 1980). Some work has been initiated by Ramirez (1981, 1982) and by Wildung et al. (1978) to develop a mechanistic model using column data but no results are available yet.

A review of the leaching information (Tables 4-6, 4-9) reveals that there is often a significant difference between column data and batch data. One of the principal reasons for this is that the liquid-to-solid ratio used in column studies is much lower than in batch studies due to compaction. The lower value of R will result in higher concentrations of most elements.

Investigators of the leaching behavior of all types of shales have noted a rapid exponential drop in the concentration of most elements over the first few pore volumes, followed by an approach toward some lower equilibrium concentration. This behavior also has been observed at field lysimeters (Garland et al., 1979), and it has been attributed to the rinsing out of readily soluble salts on or near the surface of the shale (Stollenwerk, 1980; Amy, 1978, etc.). This has been corroborated by the types of mechanistic studies described immediately above. After these salts are removed, slow dissolution of less soluble material (Stollenwerk, 1980) or pore diffusion of salts from the interior of the particles (Amy, 1978; Hall, 1982) become the controlling factor.

Stollenwerk (1980), in column experiments with Paraho and TOSCO II spent shales, observed that the concentration of TDS, B, and Mo decreased rapidly with increasing numbers of pore volumes. The pH remained relatively uniform throughout 20 pore volumes while the concentration of F remained high and/or increased (Figure 4-12). Margheim (1975) reported similar decreases in EC, Na, Ca, Mg, SO_4, and Cl. Similar results for EC and pH have been reported by Silviera et al. (1978) and for EC, by Schmehl and McCaslin (1973). Stollenwerk (1980) also noted that the slope of the straight line portion of the leaching curves for TDS, Mo, and B for the three spent shales he studied were very similar, suggesting that the same mechanism, the release of soluble salts, controls leachate concentration of these elements.

Stollenwerk (1980) also conducted a detailed study on the variation of a large number of elements in the first pore volume of leachate using a larger column. This work showed that all constituents measured decreased across the first pore volume except Ca and Si, which remained constant, perhaps reflecting their presence in a less soluble state. Thiosulfate also had an unusual leaching pattern; the highest concentrations were present in the second quarter-fraction of the first pore volume.

Biological Processes. Microbial activity within spent shale piles will affect the stability of organic residues and the mobility of trace metals through a wide range of degradation and metal transformation reactions. Microorganisms can degrade most organic and many inorganic materials, releasing a wide range of compounds into the environment. The range of functional groups released may include acids, bases, esters, amides, aldehydes, ketones, alcohols, reducing agents, and aromatic and heterocyclic molecules (McBride and Edwards, 1977). These metabolites which may be released to the atmosphere (volatilization) or into the aqueous-solid phase, will modify the chemical environment in their immediate vicinity.

Microorganisms are also capable of transforming metals through metabolism, adsorption to cell surfaces, enzymatic hydrolysis of metal complexes, oxidation-reduction reactions, alkylation reactions, and others (Brinckman et al., 1975; Iverson and Brinckman, 1978; Jewett et al., 1975; Parris and Brinckman, 1976; Huey et al., 1974, etc.). Many heavy metals and metalloids, including S, Se, Te, As, Sn, Pb, and Hg, are subject to biological methylation (Parris and Brinckman, 1976). These reactions may produce compounds which are toxic and which are stable and mobile in water and air. Probably the best known example is methylmercury.

These types of microbial transformations could release volatile compounds from the surface of spent shale disposal piles, leading to fugitive air emissions, or they could release large quantities of gas at depth in the pile, affecting its long-term stability. Additionally, they will certainly modify the chemical environment in their vicinity (Eh, pH, etc.), affecting the ultimate composition of leachates.

Some work has been initiated in this area which indicates that microbial interactions may be very important in spent shale disposal systems. Battelle PNL has studied the microbial colonization of the Anvil Points lysimeter (Garland et al., 1979). Their work has revealed that spent shale piles will be colonized by bacteria and fungi (Rogers et al., 1981b). They found that

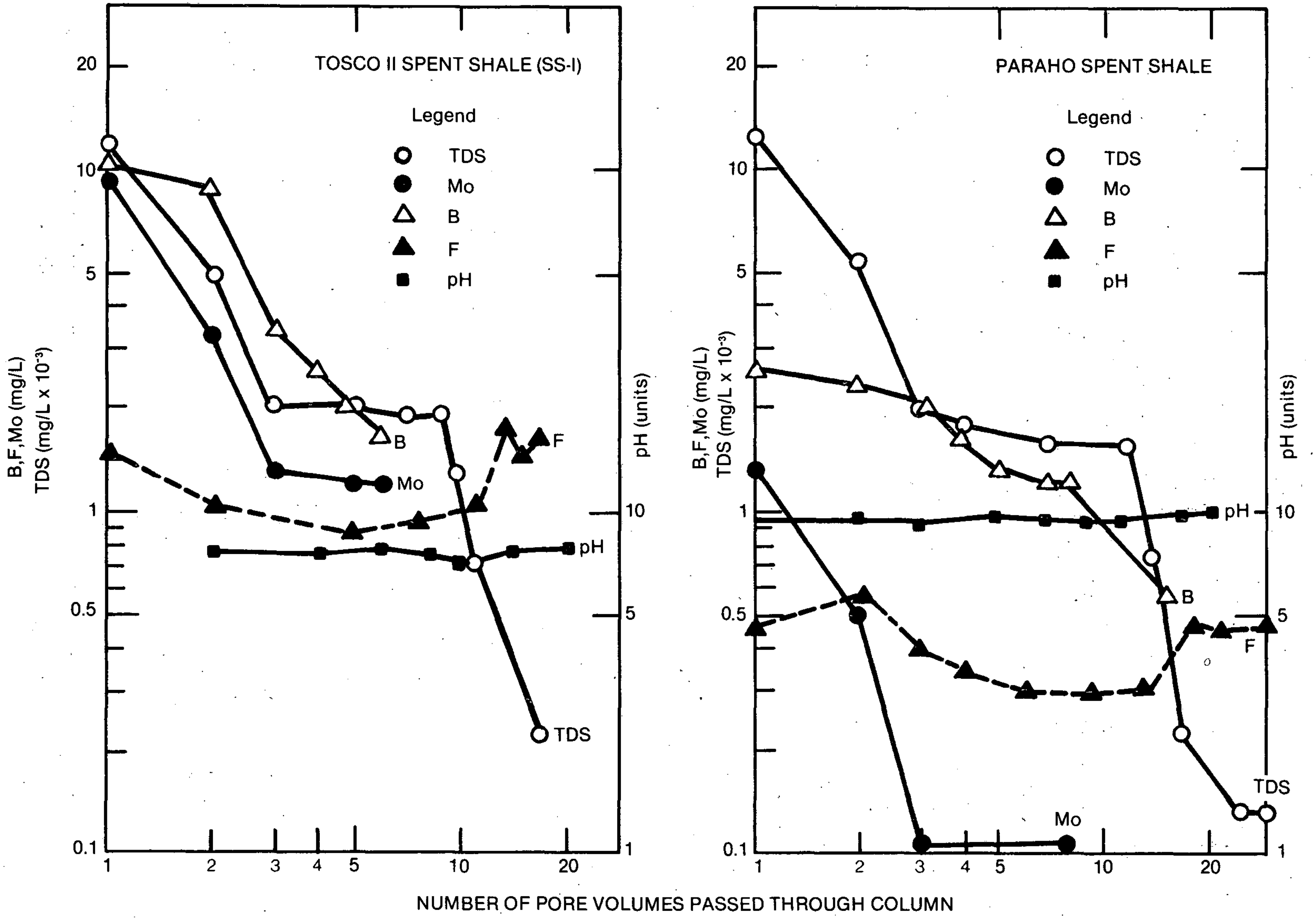

Figure 4-12. Effect of pore volume on the concentration of TDS, B, F, and Mo and on pH of leachates from TOSCO II and Paraho direct-mode spent shale (Stollenwerk, 1980).

heterotrophic bacterial populations in surface horizons of the spent shale and soil were similar in 1977. However, the bacterial populations of the shale were dominated by a single organism which used the shale as a sole source of carbon and composed 30% of the population. Laboratory culture studies revealed a dominance of Micrococcus. This dominance of a single genus indicates that, initially, spent shale is a stressed environment for microorganisms. However, in 1978 there was a greater diversity of organisms, indicating that succession of microbial populations was occurring. A core sample take in 1978 revealed that fungal and bacterial populations decreased with depth as shown in Figure 4-13. In other work, previously discussed in the codisposal section, Rogers et al. (1981a) demonstrated that microorganisms in spent shale piles can biodegrade organic acids associated with codisposed retort water.

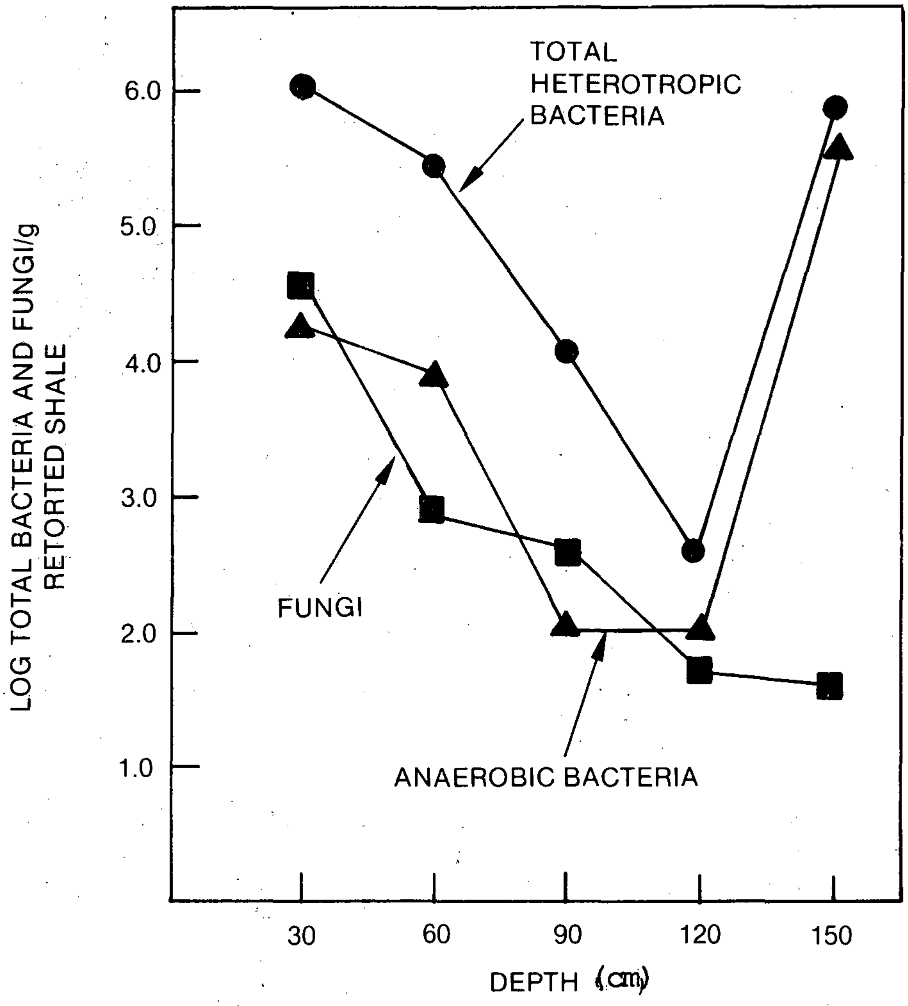

Figure 4-13. Distribution of heterotrophic bacteria, anaerobic bacteria, and fungi with depth in the Paraho spent shale lysimeter (Garland et al., 1979).

These studies indicate that if diffusion of oxygen is limited and/or if percolation of water is sufficient, subsurface levels of the pile may become anaerobic, resulting in development of microbial communities. Thus, consideration must be given to the effects of anaerobic conditions and corresponding activities of facultative and obligate anaerobic microorganisms on the solubility and chemical form of inorganic and organic residues (Rogers et al., 1981a).

In other work, Klein et al. (1981) are studying the microbial mobilization and volatilization of As in spent shale piles using laboratory culture techniques. This work indicates that microorganisms capable of utilizing spent shale as a growth medium can affect the mobility of As added as dimethylarsonic acid. Under aerobic conditions, about 2.8 μg As per 100 g shale was volatilized in three weeks. Added dimethylarsonic acid and nutrients led to the release of 152 μg As per 100 g shale under aerobic conditions and 7 μg As per 100 g shale under anaerobic conditions, in three weeks. Other work by Brierley and Brierley (1981) previously discussed (p. 4-30) strongly suggests that the decomposition of S_2O_3 in spent shale leachates is microbially mediated.

These studies clearly indicate the potential importance of microbial activity in spent shale disposal piles. This work suggests that microbes may control the pH, Eh, and chemical composition of field leachates. Thiosulfate may be oxidized, As may be mobilized from spent shale and/or co-disposed retort water (where it is present as methylarsonic acid and arsenate), and organic compounds may be decomposed to CO_2, water or other metabolites. Additional work is required on these and other microbial interactions.

ENVIRONMENTAL TRANSPORT AND EFFECTS

This section reviews studies that have considered extra-pile transport and environmental effects of surface spent shale leachates. Runoff and percolation from spent shale piles may eventually reach local surface and groundwaters. As shown in Figure 1-1, percolation or moisturization waters may move through underlying geologic materials and eventually reach alluvial and bedrock aquifers. Surface runoff, if not evaporated or collected, may reach local streams.

Proposed commercial spent shale disposal operations include stormwater drainage systems which are conservatively designed to contain the 100-yr, 30-min storm. The escape of runoff will be very unlikely and only may occur on abandonment of the project. Drainage systems could silt out if not maintained, leading to overflow.

Percolation, on the other hand, appears more significant. Subsurface drainage systems are not proposed for commercial piles due to a belief that they will be impermeable and water will not move through them, perhaps except around the toe (Metcalf and Eddy, 1975). (Liners of compacted spent shale have been proposed.) However, there is a significant body of scientific work and dogma which suggests that, over the long-term, water may percolate through these piles. Considerable additional work is required to resolve this issue, and it is not our purpose here to present a position. However, if water does percolate through the piles, either from applied water or by drainage of moisturization water, it may reach the underlying water table, contaminating underground water supplies. It is this possibility that we address.

The environmental transport of leachates in the extra-pile environment has been studied in the laboratory (Glaze, 1981; Runnells and Esmaili, 1981, 1982; Routson and Li, 1980) and in a field reconnaissance study at the Anvil Points site (Riley et al, 1981; Garland et al., 1981; Wildung et al., 1980-1981). These studies reveal a potential for contamination of groundwaters.

The significance of leachate transport in the natural environment depends on the toxic and carcinogenic properties of the leachates and any resulting modifications in natural water quality. Local surface and groundwaters in oil shale regions may be used for domestic supply, for irrigation, and for stockwatering. Chemical changes in these waters may alter their stability for these uses. This is usually assessed by comparing the resulting quality of an impacted water with various standards and criteria or by conducting long-term or short-term bioassays. The former approach was used by IWG (1980) in a risk assessment of oil shale development. The latter approach has been used by several investigators. Cleave et al. (1979, 1980) studied the effect of leachates on phytoplankton productivity, and Dickson and Adams (1980) evaluated their potential mutagenicity using the Ames test. In other work, Bergman (1980) used static, 24-hour acute bioassays to evaluate the toxicity of leachates from the Paraho field lysimeter run by CSU.

Environmental Transport

Percolates from spent shale piles may move through geologic materials beneath a spent shale pile into groundwaters. A variety of chemical, physical, and biological interactions, analogous to those affecting percolate quality in the pile environment, will modify the composition of percolates that ultimately reach the water table. These interactions may include ion exchange, precipitation, sorption, dispersion, and others.

Some laboratory, field, and modeling studies have been initiated in recent years to investigate the movement of spent shale percolates through geologic materials of the oil shale region. Most of these studies are in progress, and only preliminary results are available. However, it appears that these studies have focused on the interaction of leachates or retort water with near-surface soils, and they have investigated subsequent removal of sorbed materials by distilled water. These conditions are not representative of leachate transport in the vicinity of a spent shale pile. Percolates will exit at the base of a spent shale pile where there is no opportunity for rainfall (i.e., distilled water) to follow them. Additionally, soils will be stripped ahead of spent shale disposal and stored for later use in reclamation. Thus, subsurface, unweathered geologic materials, such as core material from the Unita Formation, should be used in future work.

Glaze (1981) investigated interactions that occur between B and F in Paraho leachates and soils from tracts C-a and C-b and from Anvil Points. He studied the mechanisms of uptake and release in column studies in which leachate application method and pH were varied. He found that the movement of B and F will be slightly retarded by soils in the Piceance Basin. Values of the distribution coefficient, k_d, were small, ranging from 8.6 to 12 mL/g for F and from 3.6 to 6.3 mL/g for B, indicating that adsorption capacity is weak. The mechanism responsible for removing B and F from the leachates depended on pH. At pH 12, the removal of B and F seemed to involve precipitation while at pH 7, they appeared to be removed by sorption on the soil. The data from these experiments were used to develop a computer model to predict B and F movement through a soil column. This work indicated that the estimated velocities of these ions through a soil column were 50 to 170 cm/yr for B and 60 to 75 cm/yr for F.

Runnells and Esmaili (1981, 1982) are extending the work of Glaze (1981) to other geologic materials (Davis Gulch soil, weathered and unweathered Uinta Formation material) and other ions (F, B, Mo, Ca, Al, As, Se, Na). They are developing sorption data from equilibrium batch studies (0.4 g/mL for 24 hrs) and continuous-flow column studies in which a "standard" large-volume TOSCO leachate is used. The resulting data will be used in a solute transport model.

Table 4-26 summarizes the distribution coefficients, k_d, for three samples of geological material when contacted with TOSCO II leachates. The distribution coefficient, which is the mass of ion sorbed per gram of solid per dissolved ion concentration, may be used to calculate the retardation of an ion due to sorption and precipitation during transport from:

$$R_f = 1 + k_d\,(\rho/\theta)$$

where ρ is the bulk dry density of the porous medium and θ is the fraction of the pore space which is saturated.

Chloride, SO_4, B, and Mo have low values of k_d which indicates that they could easily move through the soils and bedrock of oil shale regions. Fluoride, Al, and As have high values of k_d, and, thus, they would be significantly retarded by soils and bedrock of the region.

In other work, these authors demonstrated that most of the sorbed F, Mo, and B was released by distilled water rinses while As was not desorbed. It also was noted that these geologic materials provide good buffering capacity for lowering the pH of leachates from initial values near 10 to values around 8. Leachate migration also resulted in a significant decrease in hydraulic conductivity of the geologic material, presumably due to the occupation of exchange sites on clays. Distilled water rinses further decreased the hydraulic conductivity.

Others have studied the migration of inorganic (Leenheer et al., 1981) and of organic (Leenheer and Stuber, 1981) solutes in an in-situ oil shale retort water through a soil from Rock Springs, Wyoming. These studies were designed to simulate a spill of retort water rather than the movement of percolates from a spent shale pile. However, they may provide valuable insights into the migration of moisturization water (retort water) from the base of a spent shale pile. Thus, the pertinent conclusions from those studies are briefly overviewed here. (The reader should recall that spent shales may sorb some of the organic and inorganic materials from retort

TABLE 4-26

Distribution Coefficients for Selected Dissolved Species in Geologic Materials From the Colony Site (Runnells and Esmaili, 1982).

	k_d, in mL/gm								
Chemical Species	Davis Gulch Valley Bottom Soil			Weathered Uinta Formation Material			Fresh Uinta Formation Material		
	FC[b]	EC[c]	ISO[d]	FC[b]	EC[c]	ISO[d]	FC[b]	EC[c]	ISO[d]
B	1.1	nd[a]	1.7	.53	.59	1.4	.07	-.18	nd[a]
Cl	.04	-.12	-.1	.07	-.02	.57	-.25	-.31	nd
F	2.7	nd	5.3	>6.9	1.2	29	>3.5	.73	nd
HCO_3	2.9	-.12	1.0	1.7	0.0	nd	-.25	nd	nd
Mo	.53	.07	.55	.26	.13	.48	-.09	-.31	nd
Na	1.1	-.07	1.3	1.4	-.02	1.7	.4	-.05	nd
SO_4	.11	-.10	.07	.15	-.02	0.0	-.09	-.31	nd
Al	>3.9	nd	>250	>6.9	nd	>290	>3.5	nd	nd
As	>3.9	nd	14	?	nd	4.2	>3.5	nd	nd

[a] Not determined.

[b] Determined by frontal chromatography in which 13 to 30 pore volumes of standard TOSCO II leachate were percolated through column.

[c] Determined by elution chromatography in which distilled water was initially percolated through the columns followed by a slug of 10 to 20 mL of standard TOSCO II leachate, and then distilled water.

[d] Determined by batch methods in which 20 g of sample was shaken with 50 mL of standard TOSCO II leachate for 24 hrs. on a wrist-action shaker.

waters and that there is no soil layer nor opportunity for rinsing at the base of the pile.)

Leenheer et al. (1981) found that exchangeable Ca in the soil is displaced by NH_4 from the retort water and is precipitated as $CaCO_3$ by carbonates in the retort water, reducing soil permeability. A similar effect was noted by Glaze (1981). The soil adsorbed about 40% of the organic solutes in 9.5 void volumes but extracted significant quantities of natural fulvic and humic acids. The soil adsorbed NH_4, As, Ba, B, Cd, Co, Cu, F, Fe, C, Si, and Zn from the retort water. Calcium, Mg, Li, Na, K, Sr, and Mn were extracted from the soil by the retort water, and SCN did not interact and was recommended as a tracer. Leenheer and Stuber (1981) conclude that the soil was an effective adsorbent for organic solutes if less than one void volume of water is applied. More than one void volume caused migration of most of the organic solutes and extracted soil organic matter. Rainfall leaching following retort water application enhanced organic solute migration and extraction. Thus, soils may retard retort water movement if only a small amount of material is applied. These conditions may obtain for retort water migration from the base of the pile.

Work by Riley et al. (1981) suggested that alkylpyridines are less subject to sorption on soils and are more persistent during hydrologic transport than other organics in oil shale effluents. Since there is virtually no data on the sorption of these types of organic compounds, Rouston and Li (1980) studied the sorption of collidine on a Ritzville silt loam soil. This compound, a substituted pyridine, is typical of those commonly found in retort waters (Raphaelian and Harrison, 1981; Fish, 1980), and they have been identified in in situ leachates (Hall, 1982). Rouston and Li (1980) found that collidine sorption fits a Langmuir isotherm model which can be used in modeling transport of this compound. Similar work on other organic compounds present in leachates is required.

Battelle Pacific Northwest Laboratory (PNL) has/is conducting field reconnaissance studies at Anvil Points and at tract C-a to determine the effect of oil shale operations on water quality (Garland et al., 1981; Wildung et al., 1981). The Anvil Points field work has been completed, and some preliminary results for that site have been published (Wildung et al., 1980-1981; Riley et al., 1981; Garland et al., 1981). Spent shale and raw shale fines have been disposed of in this area since the 1940s, and quarterly sampling of adjacent streams and wells had been carried out by Development Engineering, Inc. (DEI) since mid-1974. The PNL study, initiated in June 1979 for two years, focused on seasonal variations in water quality. They found that well waters below the pile contained higher Li concentrations than did well water above the pile, indicating contamination from spent shale leachates. They also found significant increases in the concentration of Li and other elements in the West Sharrad stream below the shale pile (Wildung et al., 1980-1981). This was due to the discharge into the stream of contaminated seep water. No increase in the concentration of B, Mo, or F and no change in pH was found in the seep water, in contrast to expectations based on laboratory and lysimeter studies. However, elevated dissolved organic carbon (DOC) levels were found in the seep water (Wildung et al., 1981). Subsequent studies revealed that the DOC may have been from oil and retort water produced by burning of raw shale fines rather than from spent shale leachates (Riley et al., 1981).

Environmental Effects

Leachates released into the environment or stored and used on site may pose a health hazard or threat to existing water users. Discharges may degrade local water quality. Leachates stored behind catchment dams may be inadvertently used by waterfowl or wildlife, or accidental worker contact may occur.

Dickson and Adams (1980) used the Ames/Salmonella mutagenicity assay to screen extracts from Paraho, TOSCO II, and Union B spent shales. Positive mutagenic activity was detected in organic solvent extracts of all four spent shales. This result, combined with the fact that most carcinogens have been detected as mutagens in the Ames test, indicates that these extracts also may contain carcinogens. However, aqueous extracts of the same spent shales exhibited marginal or no mutagenic response, presumably because the techniques for extracting and concentrating trace quantities of these nearly water-insoluble compounds were inadequate. Additional Ames testing is required to validate this tentative conclusion.

In other work, Cleave et al. (1979,1980) used batch bioassays to study the effect of Paraho and Union B leachates on the productivity of freshwater algae indigenous to Lake Powell. They found that both spent shale leachates stimulated the growth of their test alga, Scenedesmus, and that Paraho leachates (Utah shale) were more biostimulatory than Union B leachates. These investigators concluded that Colorado River salinity levels from leachates would probably never reach high enough levels to inhibit algal growth in Lake Powell but that leachates might be biostimulatory to the algae there and may affect algal species composition.

In other work, Bergman (1980) evaluated the acute toxicity of three leachates from the Paraho lysimeter using static 24-hour bioassays in which juvenile fathead minnows and adult Daphnia pulicaria were exposed. The leachates were found to be nontoxic to both test species. This, however, does not imply that they would not be harmful to aquatic biota in long-term exposures. The high pH values exceed recommended levels. However, dilution and carbonate buffering on discharge may be adequate to lower the pH.

The potential public health effects of drinking water contaminated with oil shale leachates was estimated in a risk analysis (IWG, 1982). This study considered both surface water supplies and groundwater supplies contaminated by leachates. All of the constituents studied were, on discharge to the environment, below the threshold for known health effects, with the exception of Na. Sodium concentrations in contaminated surface water supplies exceeded the National Academy of Sciences recommended Na level of 100 mg/L. Skin cancer risk from ingestion of As was based on a linear nonthreshold dose-response model. For the conservative worst-case conditions used in this study, the increase in As concentration resulting from the discharge of leachates into public water supplies resulted in an upper bound estimate of increased individual risk of excess skin cancer of 1.5×10^{-9} to 4.7×10^{-9} per year.

In summary, leachates tested to date do not appear to cause any significant biological effects in short-term tests and public health effects appear to be insignificant. Chronic toxicity tests should be conducted. Also their potential impact on irrigation waters should be evaluated. And additional biological effects testing should be conducted to confirm the absence of any important acute biological effects.

Chapter 5

IN SITU SPENT SHALE

In situ retorting of oil shale will leave large quantities of spent shale underground where it may be leached by local groundwaters or by infiltration of precipitation (Figure 1-2). A 50,000 BPD plant based on the Rio Blanco and Occidental in situ processes (aboveground retorting accounts for 50% and 30% of the total production) will leave 46,000 ton/day and 62,000 ton/day of spent shale underground, respectively, for 96% on-stream time and 65% oil recovery. Similarly, a 50,000 BPD plant based on the Geokinetics process will leave 116,000 ton/day of spent shale underground for 96% on-stream time and 50% oil recovery. For a 20-year project life, these processes will leave a large number of chambers packed with spent shale in the underground environment. The Rio Blanco process will leave behind 340 retorts, the Occidental process will leave behind 640 retorts, and the Geokinetics process will leave behind 14,580 retorts. Pertinent supporting calculations for these three processes are summarized in Table 5-1.

IN SITU SPENT SHALE DISPOSAL PROCEDURES

These vast quantities of spent shale must be safely disposed of, i.e., abandoned, to protect local ground and surface waters. Commercial plans have not been formulated yet for the abandonment of in situ retorts, although several possibilities have been qualitatively assessed and investigated in the laboratory (Persoff and Fox 1979, 1982; Mehta and Persoff, 1980; Fox et al., 1980; Mallon, 1979). A frequently voiced industry position is that special abandonment procedures probably will not be required because the resulting spent shales are relatively isoluble and, thus, not highly leachable and because in situ sites are dry.

The issue of whether or not abandonment procedures will be required is not yet resolved and additional research and field studies are required. A clearer understanding of the relevant issues will emerge from the review of in situ leaching studies to be presented in a subsequent section. The purpose of this section is to present an environmental framework for discussing and evaluating in situ leaching research. Accordingly, important field problems will be identified and discussed, and several generic abandonment procedures which have been proposed for in situ spent shale disposal will be addressed.

The field problems which must be addressed on abandonment of in situ processes differ, depending on the retorting process and the geohydrology. Two separate in situ processes have been proposed, and each may be expected to result in different water-related environmental problems. Therefore, they will be individually discussed.

TABLE 5-1

Some Production Statistics for Three Proposed In-Situ Developments (based on data in Fox, 1980b).

	Tract C-a Rio Blanco Process	Tract C-b Occidental Process	Uinta Basin Geokinetics
Commercial production (bbl/day)	50,000	50,000	50,000
Retort size, length x width x height (ft)	300 x 150 x 750	310 x 155 x 390	200 x 200 x 30
Retort spacing (between sides x between ends) (ft)	95 x 95	150 x 50	50 x 50
Retort porosity (percent)	40	23	?
Distance from ground surface to top of retort (ft)	450	1,400	50
Retort efficiency			
In-Situ	65	65	50
Surface	90	90	N/A
Burn rate (ft/day)	14	1	1
Time to burn one retort (days)	54	390	200
Oil shale density (lb/ft^3)	137	137	137
Shale grade (gal/ton)	25	25	25
Surface retort	Lurgi	Lurgi	N/A
Days of operation per year	350	350	350
Weight of shale moved to surface,[a] 1,000 ton/retort	925	295	0
Weight of shale retorted in-situ,[b] 1,000 ton/retort	1,387	988	82
Weight of in-situ spent shale produced per day			
1,000 ton/retort[g]	943	672	56
1,000 ton/day[h]	46	62	116
Oil production,[c] 1,000 bbl/retort			
In-Situ	537	382	24
Surface	495	158	0
Number of in-situ retorts			
Total retorts started per yr[d]	17	32	729
Retorts burning simultaneously[e]	3	36	437
Surface area[f] (acres/yr)	21	41	711

[a] length x width x height x density x porosity

[b] length x width x height x density x (1-porosity)

[c] weight of shale x retorting efficiency x shale grade

[d] days of operation x total daily in-situ production/in-situ oil production

[e] $\frac{\text{time to burn one retort}}{\text{days of operation}}$ x total retorts started per year

[f] total retorts started per year x (retort surface area + pillar surface area)

[g] weight of shale x 0.68

[h] $\frac{\text{weight of spent shale per retort}}{\text{in-situ oil production per retort}}$ x daily in-situ oil production

Vertical Modified In Situ Process (VMIS)

This process has been proposed for commercial development by Occidental Oil Shale Company (C-b Shale Oil, 1977) and by the Rio Blanco Oil Shale Project (Rio Blanco, 1977). Although both developers recently have abandoned their in situ commercialization plans due to unfavorable economics, this does not preclude the future development of this technology under a different set of economic conditions. The successful deployment of this technology requires a thick, continuous, vertical section of oil shale not interrupted by significant thicknesses of barren rock (Smith et al., 1978a). The resource that best meets this criterion is the Mahogany Zone and its overlying oil shale in the Piceance Creek Basin. This region is estimated to contain some 419 billion barrels of oil amenable to VMIS recovery techniques.

The geohydrology of this region has been extensively studied (Coffin et al., 1968; Weir and Dinwiddie, 1973; Weir, 1972; Weeks et al., 1974; Welder and Saulnier, 1978; TRW, 1982). Weeks et al. (1974), in a much quoted paper, conceptualized the geohydrologic system in this region as consisting of an upper and lower aquifer separated by the relatively impermeable Mahogany Zone (Figure 5-1). Local streams were assumed to be recharged, amounting to some 80% of their flow, by water from the upper aquifer.

Occidental and the Rio Blanco Oil Shale Project have proposed to locate in situ retorts in these formations as shown in Figure 5-1. The resulting retorts would intersect one or more of the adjacent aquifers, altering predevelopment geohydrologic conditions and impacting groundwater quality. During development and retorting, aquifers adjacent to the retorts would be dewatered. However, following abandonment, groundwater would re-invade the site, filling the retorts and leaching spent shale. The leached material could be transported in local aquifers and ultimately discharged into streams and springs or pumped into wells.

This has been studied by several investigators (Fox, 1980b; Mehran et al., 1980; Robson and Saulnier, 1981) who uniformly conclude that the local and regional impacts from in situ spent shale leaching may be significant. A number of control technologies and strategies have been formulated and evaluated to alleviate these potential problems. Although none have been seriously proposed for commercialization, they are overviewed here to provide a framework for studying in situ leaching.

Control Methods

A number of strategies, including site selection, retort grouting, and intentional leaching, have been proposed for VMIS retort abandonment. Some of these also may be suitable for a Geokinetics-type process, to be discussed subsequently. Each proposed method is described briefly here. These methods have been discussed extensively and evaluated in modeling and laboratory studies

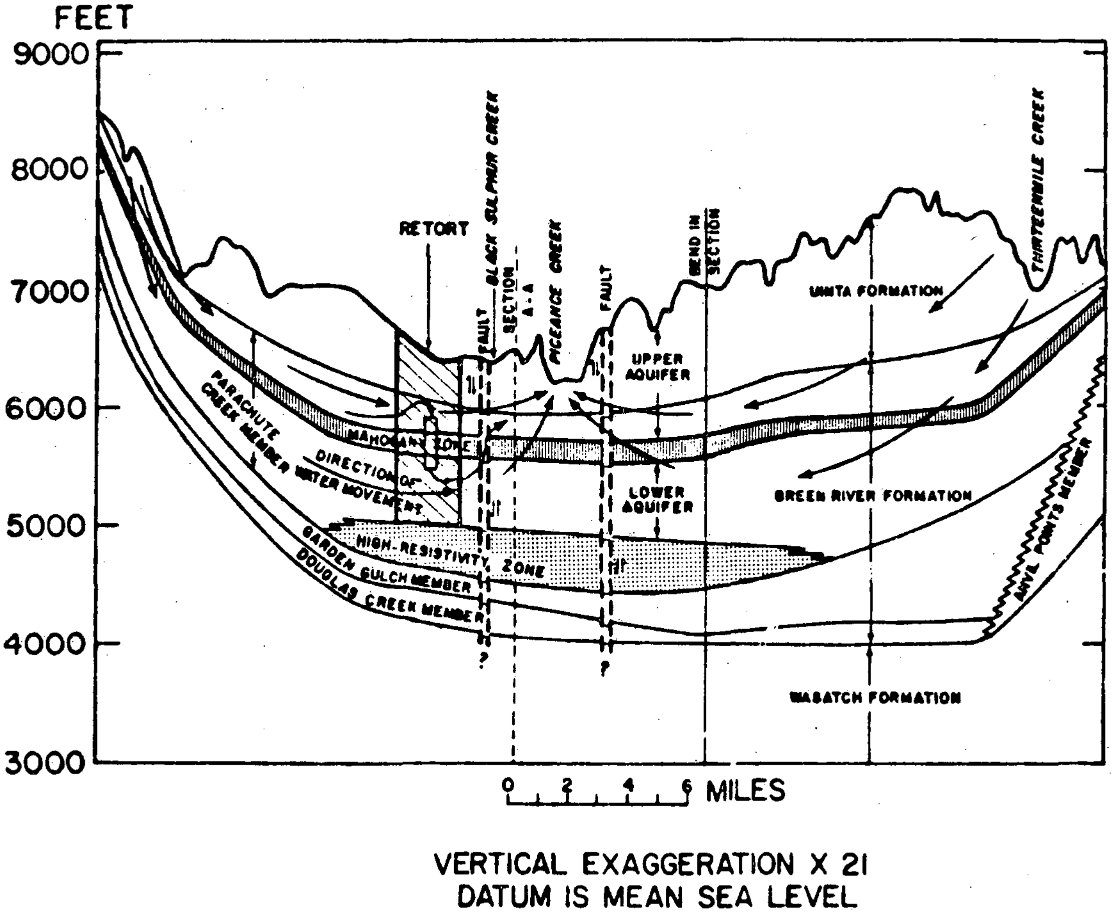

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Figure 5-1. Geohydrologic section through the Piceance Creek Basin. Adapted from Weeks et al. (1974).

reported elsewhere. The serious reader is referred to this large body of literature for additional information (Fox et al., 1980b; Persoff and Fox 1979, 1982; Mehta and Persoff, 1980; Mallon, 1979; U.S. DOE, 1979; Nevens et al., 1977).

In situ spent shale disposal procedures are based on site selection, retort plugging, hydrogeologic modifications, leaching, and various physical and chemical processes that alter the spent shale.

Site selection involves the location of a VMIS retort in a groundwater-free zone. This would minimize or eliminate in situ leachate formation and transport, and it represents the most desirable condition for protecting groundwater from degradation. Unfortunately, there is inadequate field data to evaluate this strategy over large areas, and such evaluations must be done on a case-by-case basis, during the resource evaluation phase of any commercial project.

The retort plugging strategies seek to minimize the flow of groundwater through abandoned retorts by filling them with a cementitious material to reduce permeability. The amount of leachable material present in the retorts would not be changed, but the rate of transport of leachable material into the environment would be reduced by controlling the amount of water penetrating the retort. The purpose of these strategies is to keep the concentration of pollutants in the leachate leaving the retort within acceptable limits. Technologies to plug abandoned in situ retorts include sealing with a grout manufactured from surface spent shale and in-place precipitation of calcite.

The hydrogeologic modification strategies seek to alter local geohydrologic conditions to minimize the flow of water into the retorted area. This may be accomplished by constructing a large underground wall, called a grout curtain, around a large block of retorts. This wall could divert most of the groundwater flow around the retorted area. This also could be achieved by constructing the retorts with an impervious layer, or cap rock, between the retort and adjacent aquifers or by surrounding a retorting site with a series of wells. This latter option would increase the permeability on the periphery of a retorted area, routing flow around the retort site rather than through the retorts.

The purpose of the leaching strategies is to reduce the amount of leachable material remaining in place and to meter out the balance so that the resulting concentrations are within environmentally acceptable limits. This could be accomplished by intentionally leaching the retort with mine dewatering effluents and pumping the leachate to a surface treatment plant for upgrading and final disposal. Analogously, an adsorbent or exchange resin could be pumped into the retort as a slurry to trap leachables as they form and meter them out over a period of time.

The in-situ leaching problem also may be mitigated by physically or chemically modifying the in-situ spent shale to reduce its leachability. This may be accomplished by operating the retort to produce inert silicate minerals or by using a wetting agent to reduce the wettability of the spent shale.

Geokinetics True In Situ Process

This is the only in situ process which presently is of commercial interest. It will be deployed in the Mahogany Zone of near-surface oil shale deposits characterized by an overburden thickness of less than 100 feet (Lekas 1979, 1981). Suitable deposits occur in the shallow oil shale resources in the Southern Uinta Basin which are estimated to contain some 4.9 billion barrels of oil amenable to recovery by a Geokinetics-type process (Dana et al., 1980).

A geologic cross-section through the southeastern Uinta where deposits with these characteristics occur is shown in Figure 5-2. The Parachute Creek Member outcrops at the surface in areas suitable for processing by a Geokinetics-type process. The aquifers in these regions that may be affected by oil recovery occur in the Parachute Creek Member and the Douglas Creek Member of the Green River Formation. Alluvial aquifer also occur in some regions. The location and areal extent of these aquifers are briefly overviewed here because they are less well known than the corresponding aquifers in the Piceance Basin where the VMIS technology has been proposed. Most of this discussion is taken from Law (1982); Holmes (1980); and the White River Shale Project (1977).

The principal aquifer in the Parachute Creek Member is the Birds Nest Aquifer which is a zone of cavities believed to have formed by the leaching of nahcolite. The zone is persistent laterally and vertically throughout the Uinta Basin, and its stratigraphic position corresponds approximately to the Horse Bench Sandstone in the middle of the Member (Figure 5-2). This aquifer probably would be absent in most regions suitable for a Geokinetics-type retort. Other, localized water-bearing units have been reported throughout the Uinta Basin. These are highly mineralized and discontinuous, and their presence depends on local recharge and discharge sources. One or more such "perched" aquifers associated with the Mahogany Zone has been identified at Geokinetics' Seep Ridge site, and others probably are located throughout the region.

The Douglas Creek Member underlies the retorting zone and occurs throughout the Uinta Basin. It is present at the surface in the southeastern portion of the Uinta Basin and in major stream valleys. Data are not available to identify specific water-bearing units in the upper portion of this Member, and such units are believed to include the major shallow aquifer in the Uinta Basin, the Douglas Creek Aquifer. This aquifer, which includes permeable sandstones and contains usable water, is persistent throughout the Uinta Basin, except locally where the aquifer is absent due to erosion. The aquifer ranges in thickness from about 300 to 800 feet, generally thickening from east to west.

The Geokinetics process can disturb this natural geohydrologic system through retort blasting and subsequent recontouring of the land. The Geokinetics process involves controlled blasting to introduce permeability into the Mahogany Zone. This is accomplished by uplifting the surface of the land. This process modifies the hydraulic properties of the Mahogany Zone and overlying materials and may affect the properties of underlying and horizontally adjacent materials by propagating fractures through them. This increased permeability will enhance the infiltration of precipitation through the overburden and its downward migration through the retort and underlying aquifers. The resulting leachates may move vertically downward, eventually reaching the

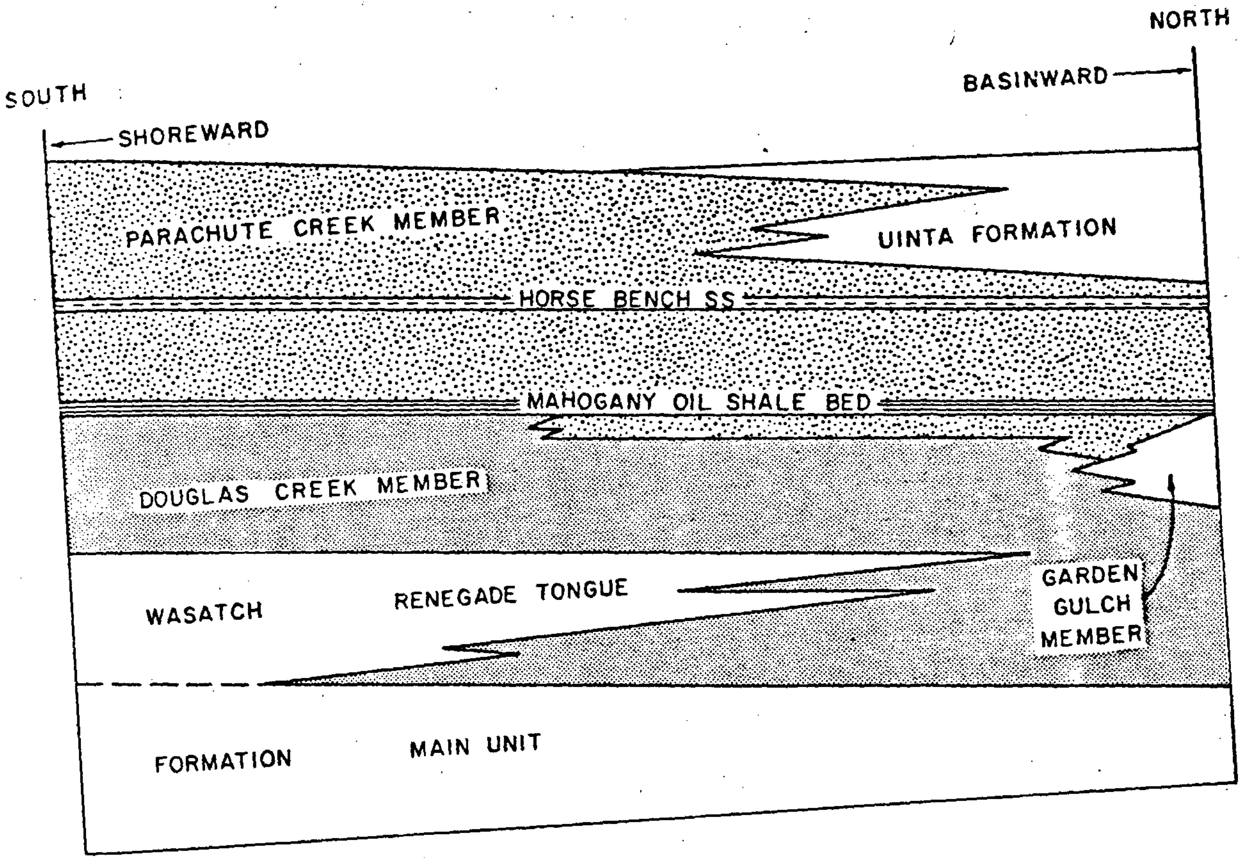


Figure 5-2. Geologic Section through the Southeastern Uinta Basin (Law, 1982).

Douglas Creek Aquifer or it may migrate horizontally, discharging at the surface through streams or springs. The specifics of leachate migration depend on site geohydrology which must be evaluated on a case-by-case basis.

Enhanced overburden permeability at the Geokinetics Seep Ridge site has resulted in gas leakage during experimental field tests. Surface treatments and modifications in blasting procedures are being studied to reduce overburden permeability. Such treatments also would help prevent precipitation recharge and leachate migration. Site reclamation procedures may include leveling of the mounds which result from surface uplift. This also would help prevent precipitation infiltration. If such treatments reduce overburden permeability below that naturally present, increased runoff and reduced recharge may occur.

Preliminary studies of retort infiltration at the Seep Ridge site (Kaman Tempo, 1981) suggest that the distance between the retort and the shallowest underlying aquifer (800 to 900 feet) and intervening zones of relatively impervious material will prevent any significant downward migration of leachates. However, this does not exclude the possibility of horizontal leachate migration through permeable zones beneath a retort. Additional studies are in progress to further evaluate any possible groundwater contamination from leachate migration at this site.

Although preliminary studies at the Seep Ridge site suggest that groundwater contamination may not be significant, other sites may have different geohydrologic characteristics which would alter this conclusion. In particular, careful attention should be focused on the location of retorts relative to alluvial aquifers, overlying aquifers, underlying aquifers, and areas of recharge and discharge. Site-specific investigations are required at each potential site to assess groundwater contamination.

IN SITU SPENT SHALE MINERALOGY

The leachability of in situ spent shales depends on the chemical and physical changes in the shale that occur during retorting and on subsequent alterations that occur during retort cooling and leaching. Each of these broad areas is separately overviewed.

Mineral Phases That Form During Retorting

The leaching of inorganic and organic materials from in situ spent shales will be influenced by: (1) chemical-mineralogical characteristics and surface properties of spent shale, (2) particle size distribution and mineral grain size of the spent shale, (3) quality and temperature of groundwater, and (4) flow regime of groundwater migrating through an abandoned retort. Work completed to date suggests that the chemistry of the spent shale and of the invading groundwater exert the most significant control over leachate composition (Peterson et al., 1982). Retorting parameters such as maximum temperature, time at temperature, retorting atmosphere, and particle size determine the final characteristics of the spent shale (Table 2-1).

The purpose of this section is to overview the mineralogical reactions that occur during in situ oil shale retorting. Similar information on the organic composition of in situ spent shales is not available. The limited available data on organics is included in the section on "Organic Composition of In Situ Leachates". Post-retorting mineralogical reactions that occur during retort cooling and leaching will be discussed in the next section. This section will use data derived from mechanistic laboratory studies to define the solid-phase reactions that occur during in situ retorting. A later section will review the mineralogy of samples and cores from experimental field retorts based on the Geokinetics and Occidental processes.

This review is not intended to be a critical analysis nor an exhaustive review of the kinetics and mineralogy of in situ spent shale. Instead, it is hoped the reader will be provided with sufficient information to understand and to interpret leaching data presented in subsequent sections. If the reader desires more detailed information on reaction kinetics and mineralogy, s/he is referred to the original literature references.

The importance of mineralogy to in situ spent shale leaching was first noted by Smith et al. (1978b) who concluded that certain slow, high-temperature reactions would produce relatively insoluble in situ spent shale, compared to surface spent shale. They demonstrated that the major elements in raw shales (K, Al, Mg, Si, Fe) are incorporated into relatively insoluble, high-temperature silicates at the temperatures (800-1000 C) encountered in in situ retorts. They also hypothesized (no experimental data were presented) that unvolatilized trace elements would be incorporated into these synthesized minerals. Subsequent work by Park et al. (1979), Kuo et al. (1979), Bethea et al. (1981), and Peterson et al. (1982) has corroborated Smith et al.'s (1978b) results that major elements are incorporated in relatively inert high-temperature silicates. However, recent investigations by Peterson et al. (1981, 1982) demonstrate that many trace elements are not incorporated in the high-temperature silicates and may be readily leached from in situ spent shales. And other work by Krause et al. (1980) demonstrates that CaO may coexist with these high-temperature products because the original shale is SiO_2-deficient. This produces high pH leachates which readily attack the otherwise inert silicate phases.

The mineralogy of spent shale depends on the original raw shale mineralogy and the effect of retorting conditions such as temperature, time at temperature, and gas composition (Park et al., 1979) on that mineralogy. A number of studies has been conducted recently on major minerals present in in situ spent shales (Kuo et al., 1979; Park et al., 1979; Smith et al., 1978b; Williamson et al., 1980; Melchior, 1980; Peterson et al., 1982) and on the effect of retorting conditions on the relative amounts of each phase (Smith et al., 1978b; Peterson et al., 1982; Park et al., 1979; Campbell, 1978; Burnham and Koskinas, 1980; Burnham et al., 1980). Other work is in progress at Los Alamos National Laboratory (LANL) to define the minor mineralogy of in situ spent shales (Peterson, 1981). All of this work has focused on modified in situ spent shales from the Lawrence Livermore National Laboratory (LLNL) or Occidental Logan Wash experimental retorts. Other work has investigated the major mineral phases present in spent shale from a Geokinetics experimental retort (Krause et al., 1980), and additional work is in progress at Lawrence Berkeley Laboratory (LBL) and the Laramie Energy Technology Center (LETC) to characterize the mineral and chemical composition of several cores from a more recent Geokinetics retort. The mechanistic studies will be briefly reviewed here to provide a framework for interpreting mineralogy and leaching data. Then, characterization data for Occidental's and Geokinetics' studies will be reviewed within this framework.

Table 2-1 summarized several important process parameters for the Occidental modified in situ process and for the Geokinetics horizontal true in situ process. These in situ processes are quite different from the surface processes. Maximum temperatures locally may reach 1000 C or higher (Campbell et al., 1981) in in situ retorts because they are contained adiabatically underground by raw shale. The time at maximum temperature may range from a day or more in the Geokinetics process up to 20 days or more in the Occidental modified in situ process. And the retorts will remain hot for long periods, perhaps years, following retorting. These long periods at high temperatures will allow certain solid-solid mineralogical reactions to reach equilibrium (Park et al., 1979). Another important difference between surface and in situ processes is the retorting atmosphere. Air (Geokinetics) or air and steam (Occidental) will be used as sweep gases rather than recycle gas which is commonly used in surface processes. Steam is used to modulate the temperature within an in situ retort, and it also improves the BTU content of the offgas while oxygen is used to combust the char behind the pyrolysis zone. These three major differences, viz., high temperatures, long times at elevated temperatures, and the presence of oxygen and steam in the inlet gas, result in significant differences in mineralogy between surface and in situ spent shales.

Two major groups of reactions may be expected to occur during in situ retorting. The first would occur in the pyrolysis zone (Figure 2-7) where the atmosphere is anoxic and temperatures may reach 500 C. The reactions expected in this zone are similar to those that occur in surface retorts, discussed previously, and include carbonate and sulfur reactions. The second major group of reactions occurs in the combustion zone of an in situ retort (Figure 2-7) where the atmosphere is oxidizing, where steam is present in the inlet gas, and where temperatures locally may exceed 1000 C. Silication reactions are dominant in this zone, although carbonate decomposition and sulfur reaction may continue to completion. Carbonates and metal oxides react with silicate to produce high-temperature silicate phases.

The carbonate and sulfur reactions that occur during in situ retorting are similar to those already discussed for surface processing. Thus, the reader is referred to Chapter 4 for information on these reactions. This section will focus on silication reactions, which are unique to in situ processing. Since the reaction pathways are uncertain, our discussion will focus on a qualitative interpretation of laboratory studies.

Silication Reactions

This discussion of silication reactions is derived primarily from data presented by Park et al. (1979, 1980) because their studies are believed to be more representative of conditions likely to occur in field in situ retorts. Park's work has demonstrated that the important high-temperature silication reactions require 10 to 100 hrs or more to reach quasi-equilibrium conditions (Figure 4-3) and most other laboratory studies used much shorter times at temperature.

Some of the important results from Park et al.'s (1979) work that are relevant to in situ processes were summarized in Figure 4-3 (only the longer residence times, >10 hrs, are important here). Additional information from that study is presented in Figure 5-3 which summarizes the steady-state mineral content for Logan Wash raw shale retorted at from 500 to 1200 C for time periods of up to 85 days.

Figure 5-3 shows that prolonged retorting, such as occurs during the Occidental and Geokinetics proceses, should lead to the complete disappearance of all dolomite and calcite by 650 C and of periclase by 800 C. However, the relative abundance of silica, dolomite, and calcite in the raw shale is important in determining the end products of the silication reactions. Krause et al. (1980) have demonstrated that if silica is deficient, free lime can coexist with the high-temperature silicates. Although Park et al. (1979) did not detect lime, this does not demonstrate that it was not present due to limitations of XRD; Krause et al. (1980) had to use high-resolution transmission electron microscopy to identify free lime.

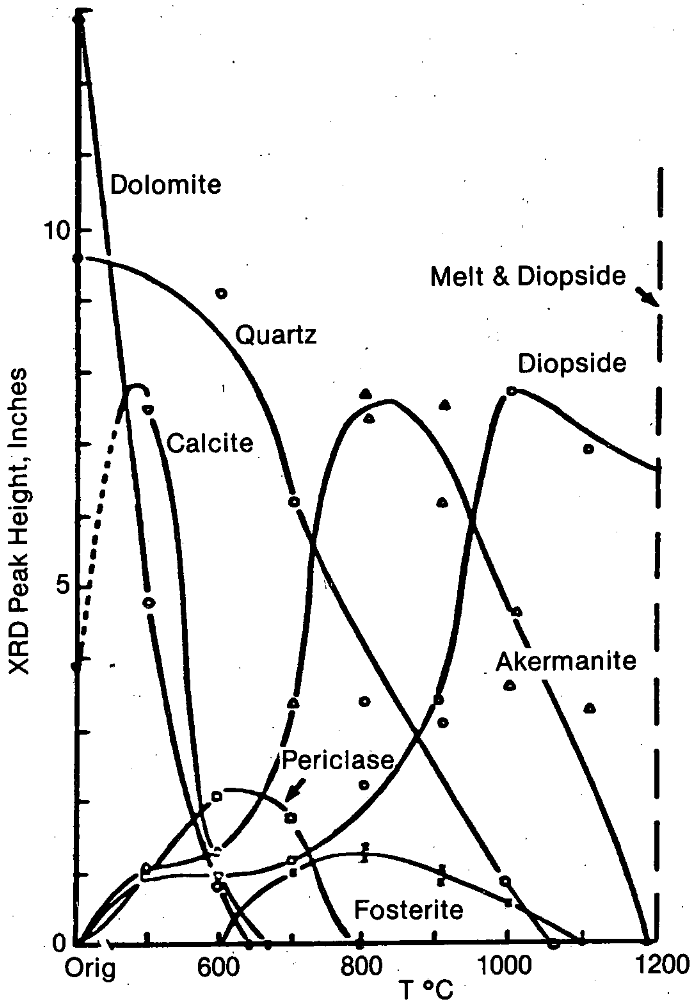


Figure 5-3. Quasiequilibrium mineral content after extended retorting (23 to 89 days) in air (Park et al., 1980).

The periclase, lime, and calcium carbonate formed by the decomposition of dolomite and calcite react with quartz to form calcium-magnesium silicates such as diopside, akermanite, and forsterite. The reaction pathways leading to these silicates are not clearly understood, but are believed to occur in several stages as a strong function of both temperature and time (Park et al., 1979). Some postulated reactions are summarized in Table 5-2. These reactions are subdivided into two major groups, depending on the temperature range in which they are important. The Group I reactions occur at lower temperatures than Group II, and they produce secondary phases that are not stable at the higher retorting temperatures. These secondary phases usually coexist with primary phases and with secondary phases that are stable at higher temperatures. The Group II reactions produce secondary phases that are stable at the highest retorting temperatures and that can be crystallized from the molten state. Some of these phases coexist with primary phases and with products of the Group I reactions.

Figure 5-3 indicates that as temperatures increase above 500 C, quartz decreases and disappears above 1000 C because of these silication reactions. Both akermanite and diopside appear around 500 C at low levels. Akermanite is the principal mineral phase between 750 and 900 C, and decreases thereafter until it disappears at the fusion temperature of 1200 C. Diopside increases gradually from 500 C to about 1000 C where it becomes the dominant mineral phase. Forsterite starts to form around 600 C, peaks at 800 C, and disappears by 1100 C. In other work, Park et al. (1981) demonstrated that steam accelerates these carbonate decomposition and silication reactions (Figure 5-4) which is consistent with results reported by Burnham et al. (1980) and Campbell and Taylor (1978).

In summary, the high temperatures, long reaction times, and steam environment of in situ retorts should result in the formation of relatively insoluble silicates. The particular suite of minerals is an indicator of the temperature that the spent shale reached.

Mineral Phases That Form During Retort Cooling and Leaching

Additional mineralogical reactions may occur after retorting ceases. Post-retorting reactions fall into three broad categories: (1) solid-phase reactions initiated during retorting; (2) reactions due to retort cooling procedures, and (3) reactions due to water seepage into the retort. The first group of reactions is covered by the material presented previously (see Figure 5-3) and is not discussed here. This section will focus on mineralogical reactions due to retort cooling procedures and water seepage into the retorts.

Oil shale is a poor thermal conductor, and vertical modified in situ retorts are completely surrounded by it. Studies have shown that these retorts may remain at high temperatures for long periods of time and that retort cooling may be required to preserve structural integrity. This is relatively unimportant for near-surface Geokinetics-type retorts which connect to the surface by a network of fractures which facilitate cooling.

Gas and water cooling have been proposed for VMIS retorts, and each method has been studied at Occidental's Logan Wash experimental site.

TABLE 5-2

Some Solid-Phase Reactions That Have Been Hypothesized to Occur in In-Situ Retorts (Krause et al., 1980).

Group I

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} \rightarrow \underset{\text{Calcite}}{CaCO_3} + \underset{\text{Periclase}}{MgO} + CO_2$$

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} + \underset{\text{Quartz}}{SiO_2} \rightarrow \underset{\text{Monticellite}}{CaMgSiO_4} + 2CO_2$$

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} + \underset{\text{Calcite}}{2CaCO_3} + \underset{\text{Quartz}}{2SiO_2} \rightarrow \underset{\text{Merwinite}}{Ca_3Mg(SiO_4)_2} + 4CO_2$$

$$\underset{\text{Calcite}}{5CaCO_3} + \underset{\text{Quartz}}{2SiO_2} \rightarrow \underset{\text{Spurrite}}{Ca_5(SiO_4)_2CO_3} + 4CO_2$$

$$\underset{\text{Calcite}}{2CaCO_3} + \underset{\text{Quartz}}{SiO_2} \rightarrow \underset{\text{Larnite}}{Ca_2SiO_4} + 2CO_2$$

$$\underset{\text{Calcite}}{CaCO_3} + \underset{\text{Plagioclase}}{3CaAl_2Si_2O_8} \rightarrow \underset{\text{Meionite}}{Ca_4Al_6Si_6O_{24}CO_3}$$

Group II

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} + \underset{\text{Quartz}}{2SiO_2} \rightarrow \underset{\text{Diopside}}{CaMgSi_2O_6} + 2CO_2$$

$$\underset{\text{Calcite}}{CaCO_3} + \underset{\text{Plagioclase}}{CaAl_2Si_2O_8} \rightarrow \underset{\text{Gehlenite}}{Ca_2Al_2SiO_7} + \underset{\text{Quartz}}{SiO_2} + CO_2$$

$$\underset{\text{Calcite}}{CaCO_3} + \underset{\text{Plagioclase}}{NaAlSi_3O_8} \rightarrow \underset{\text{Melilite}}{NaCaAlSi_2O_7} + \underset{\text{Quartz}}{SiO_2} + CO_2$$

$$\underset{\text{Calcite}}{CaCO_3} + \underset{\text{Dolomite}}{CaMg(CO_3)_2} + \underset{\text{Quartz}}{2SiO_2} \rightarrow \underset{\text{Akermanite}}{Ca_2MgSi_2O_7} + 3CO_2$$

$$\underset{\text{K-feldspar}}{KAlSi_3O_8} \rightarrow \underset{\text{Leucite}}{KAlSi_2O_6} + \underset{\text{Quartz}}{SiO_2}$$

$$\underset{\text{Plagioclase}}{NaAlSi_3O_8} + \underset{\text{K-feldspar}}{KAlSi_3O_8} \rightarrow \underset{\text{Nepheline}}{2(Na,K)AlSiO_4} + \underset{\text{Quartz}}{4SiO_2}$$

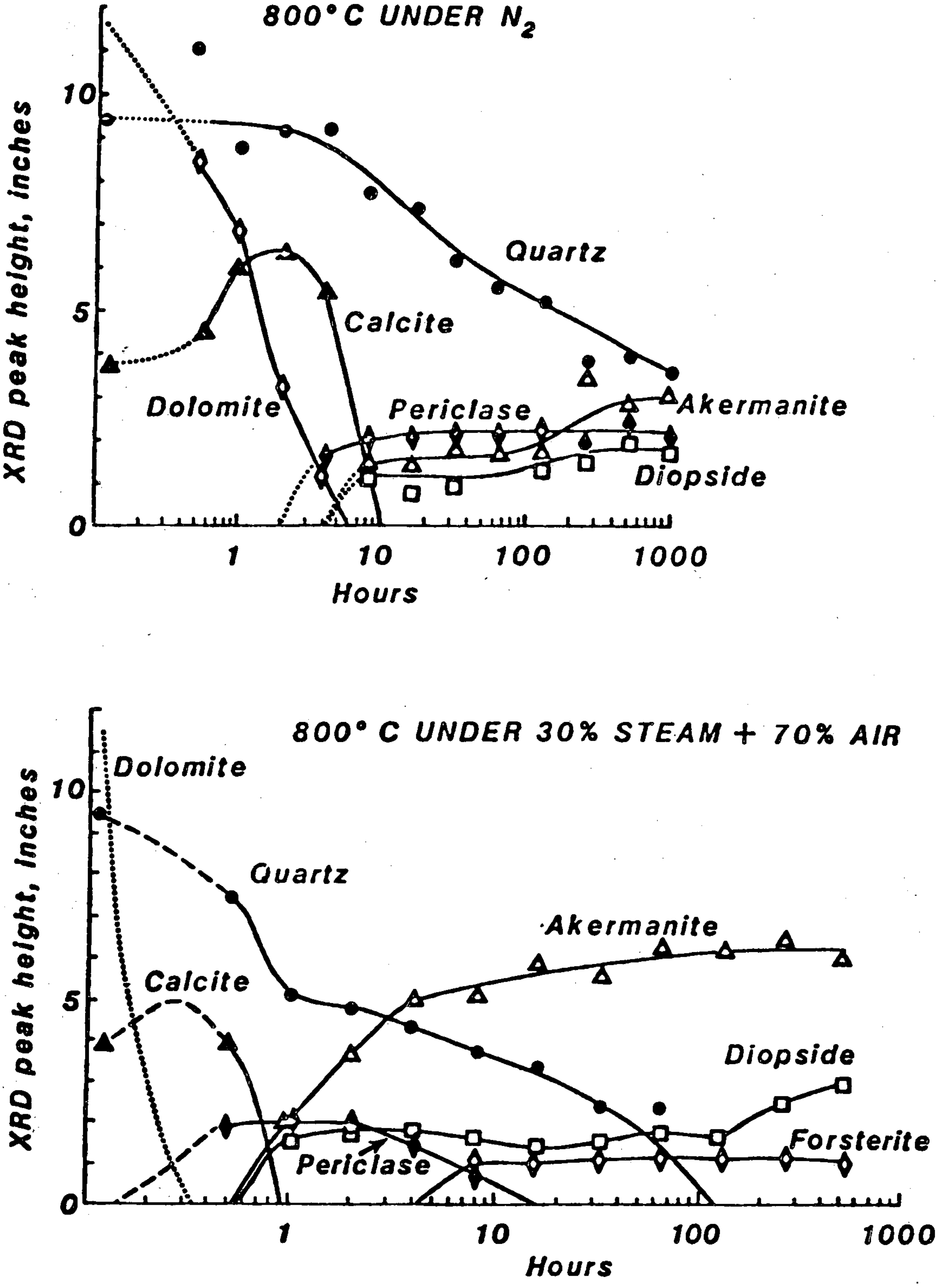


Figure 5-4. X-ray diffraction peak heights in inches versus time for isothermal retorting experiments at 800 C under 100% N_2 and 30% steam plus 70% air atmospheres (Park et al., 1980).

These post-retorting treatments are known to affect the final mineral assemblages (Peterson et al., 1982) but the precise reactions that occur have not been studied. No laboratory investigations have been conducted on the effect of cooling procedures on spent shale mineralogy. Thus, only qualitative observations, based on analyses of cores through Occidental retort 3E, are presented here.

Recycle gas and waters used during cooling supply sulfate, carbonate, and other ions which react with spent shale to form regeneration products. Sulfur dioxide in the offgas is known to react with CaO and MgO in spent shale to produce $CaSO_4$ and $MgSO_4$ (Fuchs et al., 1978; Taylor et al., 1982). Carbon dioxide in seepage waters, recycle gas, or other waters used to cool the retort will recarbonate lime, and aragonite will be the preferred form precipitating from warm solutions. These and other mineral phases, including magnesite, goethite, and calcite have been identified in field samples.

Mineral Phases Identified in Spent Shale From Commercial Processes

These mechanistic studies will now be compared with actual measurements on spent shales from field retorts. Several investigators have reported mineralogical analyses for three cores from Occidental's Logan Wash Retort 3E (Peterson et al., 1982; Kuo et al., 1978, and Park et al., 1980). Other studies have reported mineralogical analyses for cores through Geokinetics Retort 11, for samples from a trench through Retort 1 (Krause et al., 1980), and for cores from Retort 16 (Mason and Sinks, 1982). Some of their analyses are presented in Table 5-3.

These data indicate that spent shale from in situ retorts is highly heterogenous compared to surface spent shales. Nonuniformities in the raw shale bed (i.e., in particle size, void distribution, etc.) lead to nonuniform retorting, and channeling is a common problem. Therefore, spent shales from a given retort may have been exposed to widely varying retorting conditions. Other differences are introduced in the final spent shale by natural variations in the raw shale mineral assemblages. These differences are expressed in the wide range in minerals encountered in cores from field retorts. The minerals identified in in situ spent shales have been sorted into five distinct groups, based on retorting and post-retorting conditions believed responsible for their formation (Table 5-4). Each group is discussed separately within the framework of proposed reactions discussed previously.

Thermally Unstable Raw-Shale Minerals

The first group of minerals present in Table 5-4 is thermally unstable, and they decompose between 300 C and about 800 C. Analcime, the first of these to decompose, looses its water of hydration at relatively low temperatures, around 300 C, collapsing its lattice slightly (Johnson et al., 1975). It is completely incorporated in new solid phases by 700 C (Smith et al., 1978b) to 800 C (Burnham et al., 1980). Illite similarly looses its water of hydration over the range of 650 to 850 C (Smith, 1980b). Both illite and analcime may yield oxides on the loss of water.

Carbonate decomposition has been extensively studied (Campbell, 1978; Burnham and Koskinas, 1980; Burnham et al., 1980; Park et al., 1979; Smith

TABLE 5-3

X-Ray Diffraction Analyses of Spent Shale Samples From Geokinetics Retort 1 (Weight %) (Krause et al., 1981).

	SAMPLE																
	Zone 1			Zone 2			Zone 3			Zone 4			Zone 5			Zone 6	
	Not Leached	Leached		Not Leached	Leached		Not Leached	Leached		Not Leached	Leached		Not Leached	Leached		Leached	
Composition		-10M[a]	-1 in.[b]		-10M[a]	-1 in.[b]		-10M[a]	-1 in.[b]		-10M[a]	-1 in.[b]		-10M[a]	-1 in.[b]	-10M[a]	-1 in.[b]
								Primary									
Dolomite $CaMg(CO_3)_2$	26	20	25	-	-	-	-	-	-	-	-	-	-	-	-	66	57
Calcite $CaCO_3$	16	14	13	4	5	3	-	-	-	-	-	-	-	-	-	7	13
Quartz SiO_2	16	16	17	12	12	18	3	2	1	-	-	-	5	4	2	16	15
Plagioclase $(Na,Ca)Al(Al,Si)Si_2O_8$	15	14	11	18	17	24	10	9	10	-	-	-	14	8	-	7	10
K-feldspar $KAlSi_3O_8$	5	5	5	3	10	5	6	9	10	-	-	-	8	6	4	4	5
Illite-Mica Phyllosilicate	4	9	5	-	5	5	-	-	-	-	-	-	-	-	-	-	-
Montmorillonite-Chlorite Phyllosilicate	-	2	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
								Secondary									
Periclase MgO	-	-	-	12	15	8	6	5	7	-	-	-	17	11	18	-	-
Diopside $CaMgSi_2O_6$	-	-	-	24	19	24	28	33	25	30	32	20	7	1	1	-	-
Melilite-Gahlenite-Akermanite $(Na,Ca)Ca(Mg,Al)(Si,Al)SiO_7$	-	-	-	14	10	10	30	31	30	54	42	54	3	2	2	-	-
Nepheline $(Na,K)AlSiO_4$	-	-	-	-	-	-	-	-	-	4	9	8	-	-	-	-	-
Leucite $KAlSi_2O_6$	-	-	-	-	-	-	-	-	-	6	9	8	-	-	-	-	-
Scapolite (Meionite) $Ca_4Al_6(SiO_4)_6(CO_3)$	-	-	-	-	-	-	-	-	-	1	1	2	-	-	-	-	-
Idocrase (Vesuvianite) $Ca_{10}Mg_2Al_4(SiO_4)_5$-$(Si_2O_7)_2(OH)_4$	-	-	-	-	-	-	-	-	-	2	2	2	-	-	-	-	-
Illmenite $FeTiO_3$	-	-	-	-	-	-	-	-	-	1	2	3	-	-	-	-	-
Spurrite $Ca_5(SiO_4)_2(CO_3)$	-	-	-	8	5	-	3	2	4	-	-	-	22	39	46	-	-
Merwinite $Ca_3Mg(SiO_4)_2$	-	-	-	-	1	2	3	2	5	-	-	-	16	16	13	-	-
Larnite Ca_2SiO_4	-	-	-	4	-	-	-	-	-	-	-	-	8	12	13	-	-
Monticellite $CaMgSiO_4$	-	-	-	-	-	-	8	4	5	-	-	-	-	1	1	-	-
Goethite $FeO(OH)$	-	-	-	-	1	1	-	3	3	-	-	-	-	-	-	-	-
Amorphous	14	18	20	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unidentified	4	2	2	1	-	-	3	-	-	2	3	3	-	-	-	-	-

[a] Batch leach tests were performed on 50 g of -10 mesh spent shale in 125 ml deionized water (t = 2 weeks).

[b] Column leach tests were performed on 200 g of -1 inch spent shale.

TABLE 5-4

Principal Minerals Identified in In-Situ Spent Shales[a]

I. THERMALLY UNSTABLE RAW SHALE MINERALS	
Analcime	$NaAlSi_2O_6 \cdot xH_2O$
Dolomite-Ankerite	$(Mg,Fe)Ca(CO_3)_2$
Calcite	$CaCO_3$
Illite	$KAl_2(Si_3Al)O_{10}(OH)_2$
Pyrite	FeS_2
II. THERMALLY STABLE RAW SHALE MINERALS	
Quartz	SiO_2
Na-feldspar	$NaAlSi_3O_8$
K-feldspar	$KAlSi_3O_8$
III. DECOMPOSITION PRODUCTS	
Periclase	MgO
Calcite	$CaCO_3$
Wustite	FeO
Hematite	Fe_2O_3
Magnetite	Fe_3O_4
Pyrrhotite	$Fe_{1-x}S$
Gypsum	$CaSO_4$
Starkeyite	$MgSO_4$
IV. HIGH-TEMPERATURE SYNTHESIS PRODUCTS	
Augite	$(Ca,Mg,Fe,Ti,Al)_2(Si,Al)_2O_6$
Akermanite	$Ca_2Mg(Si_2O_7)$
Gehlenite	$Ca_2Al_2(SiO_7)$
Melilite	$NaCaAlSi_2O_7$
Kalsilite	$K(AlSiO_4)$
Monticellite	$CaMg(SiO_4)$
Forsterite	$(Mg,Fe)_2(SiO_4)$
Diopside	$CaMg(Si_2O_6)$
Larnite	Ca_2SiO_4
Nepheline	$(Na,K)AlSiO_4$
Leucite	$KAlSi_2O_6$
Wollastonite	$CaSiO_3$
Merwinite	$Ca_3Mg(SiO_4)_2$
Spurrite	$Ca_5(SiO_4)_2(CO_3)$
Nosean	$Na_8Al_6(SiO_4)_6(SO_4)$
V. REGENERATION PRODUCTS	
Magnesite	$MgCO_3$
Aragonite	$CaCO_3$
Calcite	$CaCO_3$
Gypsum	$CaSO_4 \cdot 2H_2O$
Goethite	$FeO(OH)$

[a] Summarized from data presented at Smith et al. (1978b); Smith (1980b); Park et al. (1981); Williamson et al. (1980); Peterson et al. (1982); and Krause et al. (1980).

et al., 1978b) because the reactions are endothermic and adversely affect the process energy balance. The principal reactions were summarized in Table 4-2 and discussed in Chapter 4.

Pyrite reactions are not as well understood as the carbonate reactions and also were summarized in Chapter 4. Smith et al. (1978b) and Burnham et al. (1981) have proposed that pyrite is reduced to hydrogen sulfide and pyrrhotite in in situ retorts. Burnham et al. (1981) and Taylor et al. (1982) further proposed that steam and oxygen may oxidize both pyrite and pyrrhotite to iron oxides. These hypotheses are consistent with mineralogical studies of in situ spent shales. Neither of these phases (Fe_2, FeS) has been identified in simulated in-situ spent shales (Smith et al., 1978b, Park et al., 1979; Williamson et al., 1980) and pyrrhotite was identified in only a few field samples from Retort 3E (Park et al., 1979).

Williamson et al. (1980) measured the iron minerals pyrite, pyrrhotite, ankerite, hematite, and magnetite in raw shale and two spent shales produced during high temperature simulated in situ combustion in the LLNL retort. This work showed that pyrite and pyrrhotite were absent in the spent shales and that hematite and magnetite were present. This suggests that pyrite and pyrrhotite are oxidized to iron oxides.

Thermally Stable Raw-Shale Minerals

The second group of minerals shown in Table 5-4 do not decompose during in situ retorting; they participate directly in solid-phase reactions (Smith et al., 1978b; Park et al., 1979). Original quartz plus new quartz formed by the decomposition of some of the Group I minerals react with metal oxides (MgO, CaO, FeO, etc.) to form high-temperature silicates of the type shown in Group IV (Burnham et al., 1980). K- and Na-feldspar, on the other hand, remain relatively stable up to about 900 C. These two distinct phases react together at 900 C, creating a new unidentified feldspar crystal (Burnham et al., 1980; Smith et al., 1978b). The quantity of the new combined feldspar then decreases between 900 and 1100 C, probably participating in the silication reactions (Smith et al., 1978b).

Decomposition Products

The third group of minerals in Table 5-4 is the decomposition products of the Group I minerals. Periclase and calcite both result from the decomposition of dolomite while wustite, hematite, and magnetite result from the oxidation of FeS and FeS_2 by steam and air (Burnham et al., 1981; Taylor et al., 1982) or the decomposition of ankerite (Williamson et al., 1980). As noted in the discussion of the Group I minerals, pyrrhotite probably originates from the reduction of pyrite by hydrogen and organics or from the oxidation of pyrite by steam. Gypsum and starkeyite originate from the reaction of carbonates and oxides with sulfur dioxide according to the reaction presented by Taylor et al. (1982) and shown in Chapter 4.

High-Temperature Synthesis Products

The fourth group of minerals in Table 5-4 is the high-temperature silicate synthesis products. As previously discussed, the silicates form from the reaction of metal oxides and carbonates with silicates. These reactions are exothermic and are slow, requiring long times to reach equilibrium (Park et al., 1979). Steam in the inlet gas greatly accelerates silicate formation, allowing the less endothermic reactions to occur at lower temperatures. The final products are relatively insoluble in water and environmentally inert compared to oxides and carbonates (Burnham et al., 1980; Smith et al., 1978b). Therefore, the presence of this suite of minerals in spent shales will tend to minimize the leaching problem, compared to surface spent shales. However, the fate of minor elements, such as Mo and F, is presently uncertain and requires additional study.

Regeneration Products

The final group of minerals is the regeneration products formed by post-burn treatments. Abandoned in situ retorts may require water or gas cooling to promote structural stability. Retort 3E, which was a principal source of core material under discussion here, was cooled by recycle gas with high CO_2 content. Water also was injected to produce steam. These and other post-burn treatments, such as the seepage of high-carbonate groundwaters into the retorts, supply sulfate, carbonate and other ions which form regeneration products. Aragonite, which was identified in Retort 3E samples, is the preferred crystalline form of calcium carbonate precipitating from warm solutions (Peterson et al., 1982). Some calcite also may have precipitated after cooling because of the high alkalinity of groundwater seeping into the retort. Gypsum also may be formed during post-burn treatment or during recycling of offgas. Sulfur dioxide in the offgas is known to react with CaO in the spent shales to form gypsum (Fuches et al., 1978; Taylor et al., 1982).

IN SITU SPENT SHALE LEACHATE

In in situ retorting, large chambers of spent shale and allied mining and processing works, including shafts, adits, drifts, and sumps, are left underground where they may be leached by groundwaters. Soluble materials then may be transported in local aquifers, withdrawn in wells, or discharged in local springs and streams.

This issue has been investigated in a number of modeling studies (Mehran et al., 1980; Robson and Saulnier, 1981; Brown et al., 1977) and laboratory studies (Stollenwerk, 1980; U.S. DOE, 1980; Jackson et al., 1975; Peterson et al. 1981, 1982; Amy, 1978; Amy and Thomas, 1977; Amy et al., 1980; Hall, 1982; Fox, 1982a; Bethea et al., 1981; Kuo et al., 1979; Parker et al. 1976, 1977; Krause et al., 1980; Leenheer and Stuber, 1977).

Early studies (Jackson et al., 1975; Amy, 1978; Parker et al., 1977) and analyses based on them (Fox, 1979; Fox, 1980b) suggested that high concentrations of TDS and certain trace elements would be leached from in situ spent shales and transported in local aquifers, posing a health and economic problem to local water users in the Upper Colorado River Basin. These early conclusions were based on leaching studies conducted on simulated spent shales (Amy, 1978; Jackson et al., 1975; Parker et al., 1977) that are now known to be chemically different from field samples (Smith et al., 1978b, Burnham et al., 1980; Park et al., 1979) and on unrealistic laboratory simulations of field conditions in which distilled water and very small particle sizes were used.

Recent studies at LANL (Peterson et al. 1981, 1982) demonstrate that the impact of in situ leaching on groundwater quality may be less significant than previously believed. These studies confirm earlier work by Park et al. (1979) and Kuo et al. (1979) that high temperatures and long times at temperature common in in situ retorts, 80 C to 1000 C for days to years, decrease the solubility of most elements studied by about an order of magnitude. Among the important trace elements, only V showed increased solubility at elevated temperatures. These studies also indicate that secondary solubility controls may actually improve groundwater quality by providing anions such as sulfate or carbonate which precipitate many toxic metals present in both groundwaters and leachates. The LANL work suggests that of the elements studied, only V, Se, and Pb may pose an environmental hazard.

Published literature on laboratory in situ leaching studies is summarized in Table A-3. These studies have been conducted using core material from Occidental's Logan Wash site, from Geokinetics' Book Cliff site, from LLNL and LETC simulated in situ retorts, and from small laboratory reactors. Other work is in progress (Bates, 1981; Stover, 1981; Sharrer, 1981). Colorado State University will study the leaching behavior of several spent shale cores from Geokinetics' Retort 16 during 1982 (Bates, 1981). Geokinetics, Inc. is conducting a field program to monitor the migration of leachates at their Seep Ridge site (Sharrer, 1981). Occidental also is monitoring leachate migration at their Logan Wash site, and they are studying organics in leachates from core 3E material (Stover, 1981). The investigations (Table A-3) include characterization, field migration, and mechanistic studies. Each type of study will be discussed in a separate section.

CHARACTERIZATION OF IN SITU LEACHATES

Accurate chemical characterizations of leachates are necessary to assess the impact of in situ retorting on groundwater quality. It is difficult to obtain reliable data because the technology is in transition, and representative samples have not been available for study. The majority of early work on in situ spent shales utilized samples from pilot-scale, simulated in situ retorts operated by LLNL and LETC or from laboratory reactors. Subsequent work on the effect of retorting conditions on mineralogy (summarized in a previous section) and on leachability indicated that materials from these early retorting experiments were not representative of in situ processes and, in fact, often more closely approximated surface reotrts. Thus, the early characterization work based on simulated and laboratory spent shales is not presented here. However, these same studies do provide valuable information on the chemistry and physics of the in situ leaching process. Data based on simulated and laboratory samples will be presented in a subsequent section on "Leaching Mechanisms."

The purpose of this section is to summarize the most accurate information presently available on the inorganic and organic composition of leachates from in situ processes. This review will be based primarily on the Occidental MIS process and the Geokinetics horizontal true in situ process. Some of the first field samples from these retorts were made available in 1977 (Geokinetics Retort 1 and 11) and in 1979 (Occidental Retort 3E). Although these materials are from early, small experimental field retorts and are thus not representative of commercial processes, the conditions experienced in them should span the range of those that will encountered in commercial processes. These materials have been the subject of intensive laboratory studies, and the results are just beginning to emerge. This section will summarize published characterization data from those studies.

Inorganic Composition of In Situ Leachates

The inorganic quality of leachates from Geokinetics' Retorts 1 (Leenheer and Stuber, 1977; Krause et al., 1980) and from Occidental's Retort 3 (Peterson et al. 1981, 1982; U.S. DOE, 1980; Stollenwerk, 1980; Fox, 1982a) has been studied. The important results from these studies are summarized in Tables 5-5 and 5-6. Each process is individually discussed.

Occidental

Spent shale samples from three coreholes through Occidental's Retort 3E have been studied. This was a small experimental retort measuring 32 feet square by 113 feet high. The input gas was 70% air and 30% recycle gas, and the retort was cooled for two weeks following retorting by cycling offgas through it. Some water was periodically injected during retorting to produce steam. A commercial process will probably use an air/steam mixture as the sweep gas; post-retorting treatments are uncertain, and either will not be required, or may include water or air cooling, rather than recycle gas cooling. (As we will discover later, recycle gas significantly affects the concentrations and types of organics present in leachates.)

Three cores from this retort have been studied. Most of this work was conducted on core 3E1, the first core to be collected (Kuo et al., 1979; Stollenwerk, 1980; U.S. DOE, 1980). These initial studies suggested that core retrieval methods had contaminated the samples (U.S. DOE, 1980), and two additional cores were collected using modified methods. Drilling agents (pipe dope, foam, and surfactants) were used to recover core 3E1. We assessed the effect of these on core leachates by comparing the average leachate concentration of 29 parameters as reported by Peterson et al. (1982) and U.S. DOE (1980) for the three cores. We found that the concentrations of Al, Fe, TOC, and conductivity were an order of magnitude higher in leachates from core 3E1 than from the other two cores. All other parameters for these three cores agreed to within a factor of two to three. We then compared these averages to the composition of the drilling agents reported in U.S. DOE (1980). This revealed that Al, Fe, and TOC were uniquely elevated in the Poly D-1000 polymer used in drilling. Thus, we believe that core 3E1 was contaminated during recovery, and we will focus on characterization results for cores 3E2 and 3E3.

The utility of these core samples (3E2, 3E3) for leaching studies has been questioned. Smith (1980b) pointed out that low sample recoveries, contamination, and scaling make interpretation of leaching studies difficult. Less than 20% of the available material was recovered from each section, and water was used as the drilling fluid. Leenheer and Stuber (1977) have cautioned that such water may alter the leaching characteristics of spent shale. They noted that some samples of Geokinetics spent shale dissolved and disaggregated when contacted with water. Finally, material from overlying segments was probably dislodged as the drill bit was retrieved, mixing material from various sections (Smith, 1980b). The representativeness of these samples of a commercial VMIS process also is questionable. Retort 3E used recycle gas retorting with intermittent steam, and it was cooled with recycle gas. None of these is representative of anticipated commercial conditions. Thus, the reader is cautioned that leaching data from Retort 3E cores, while indicative of general trends, do not represent a commercial VMIS process.

The composition of leachates from Retort 3E is summarized in Table 5-5 from several studies. The reported ranges correspond to different core sections. The mineral controls responsible for these concentrations will be discussed in the section on leaching mechanisms. These data indicate significant variability in leachate composition. This is related to the heterogeneity of spent shale caused by channeling during retorting (Peterson et al., 1982). Similar heterogeneity was noted in Geokinetics samples by Leenheer and Stuber (1977).

The pH of these leachates (cores 3E2, 3E3) ranges from 8.78 to 11.7, and the conductivity ranges from 330 to 6,990 µmhos/cm. The major cations for which data are reported are Na, K, and Ca, and the trace elements which occur at the highest concentrations are F, B, Sr, Li, Mo, and V. In other work, Fox (1982a) determined that the principal arsenic species were methylarsonic acid and arsenate. These results are very similar to those previously discussed for surface spent shales. This is due primarily to the wide range in retorting conditions experienced by various core segments. Some samples were unretorted, others were pyrolyzed only, and still others had been oxidized at high temperatures. To evaluate the effect of retorting conditions individual core segments with well defined retorting histories are required; these have not been available and a later section will try to infer trends.

Geokinetics

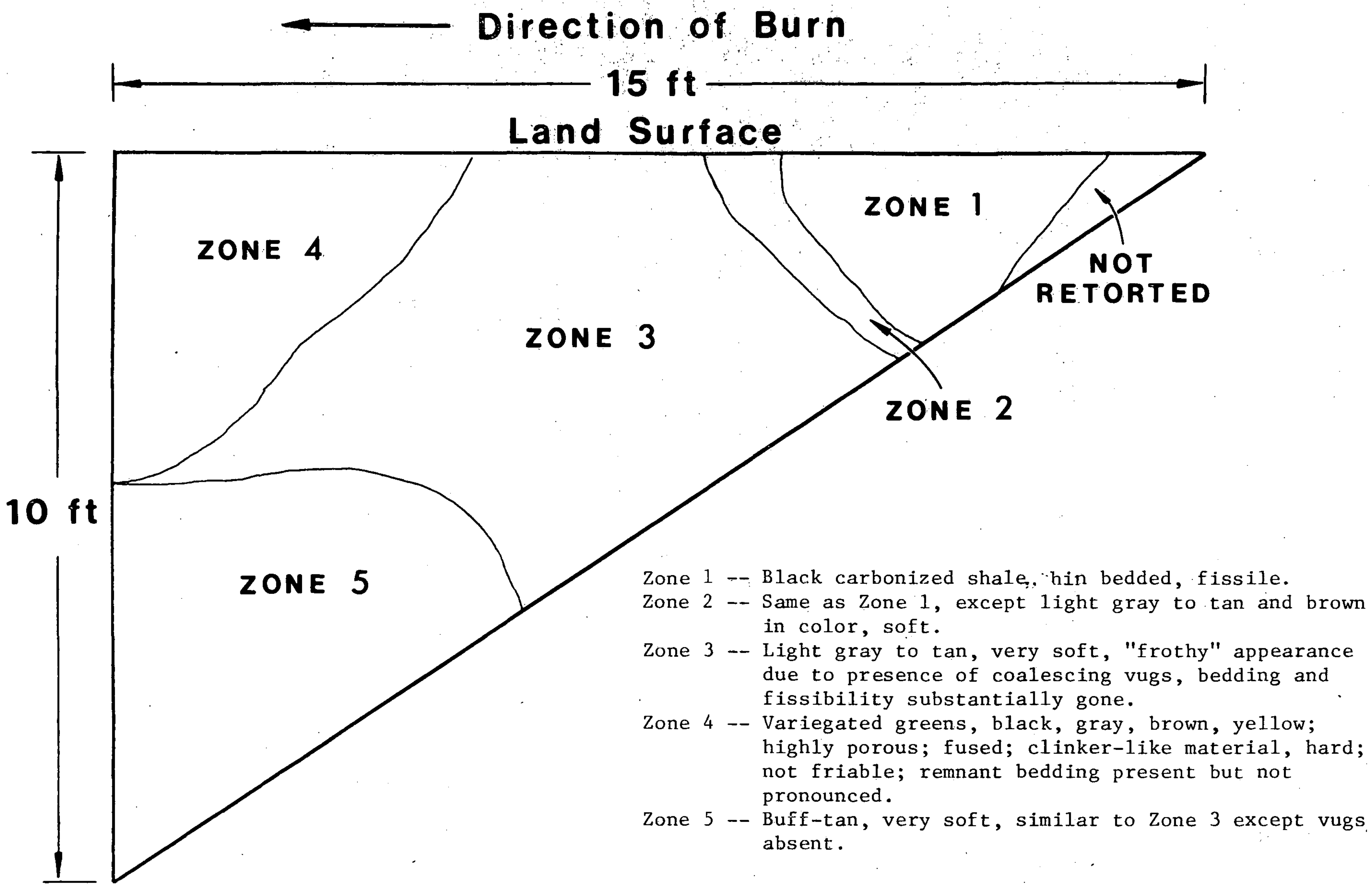
Leaching studies have been conducted only on spent shales from the first experimental Geokinetics retort, designated Retort 1 (Leenheer and Stuber, 1977; Krause et al., 1980). Although other leaching data on Geokinetics spent shale have been reported by Cleave et al. (1980), the source of their sample was not indicated. Mineralogical analyses have been reported for spent shales from other Geokinetics retorts (Retorts 11 and 16) (Krause et al., 1980; Mason and Sinks, 1982). However, we are not aware of any published leaching studies that have used these samples.

Retort 1 was drilled and blasted in July 1975 and ignited in September 1976. The retort had dimensions of 10 x 50 feet (compare these with projected commercial dimensions recorded in Table 5-1), no overburden was present, and air was used as the sweep gas (Lekas, 1979). This retort was sampled by digging a 4-foot-wide trench the full 10-foot depth of the retort. Five distinct zones were delineated, based on physical appearance, and samples from each zone were individually leached (Figure 5-5). The zones were not as homogenous as suggested by Figure 5-5. There was evidence of burn propagation along fractures, especially in zone 3. The mineralogical analyses of leached and unleached samples from each zone were presented in Table 5-3.

TABLE 5-5

Inorganic Composition of Leachates From Occidental's Retort 3E, Logan Wash, Colorado (mg/L).

	U.S. DOE,1980	Stollenwerk,1980	Peterson et al., 1981		
	Core 3E1 (PNL Data)	Core 3E1	Core 3E1	Core 3E2	Core 3E3
Al	-	-	<0.2 - 6.8	0.022 - 1.22	0.022 - 1.22
As	-	0.01 - 0.16	0.005 - 0.200	<0.002 - 0.02	<0.002 - 0.034
B	1.9 - 46	2.1 - 7.6	<0.3 - 6.7	0.262 - 6.55	0.171 - 13.0
Ba	-	-	-	0.028 - 2.80	0.020 - 0.96
Be	-	-	-	<0.001 - <0.006	<0.001 - <0.002
Ca	11 - 513	16 - 920	6 - 1,340	3.54 - 566	1.6 - 293
Cd	-	-	-	<0.014 - <0.081	<0.02 - 0.03
Co	-	-	<0.04 - 0.07	<0.002 - 0.017	<0.01 - 0.03
Cu	-	-	<0.02 - 0.04	<0.002 - 0.017	<0.001 - 0.012
DOC	152 - 2,455	-	-	-	-
DIC	30 - 280	-	-	-	-
EC, µmho/cm	1,300 - 15,000	3,340 - 12,170	-	330 - 2,780	560 - 6,990
F	-	1.2 - 11	0.8 - 22.5	0.3 - 21	1 - 31
Fe	-	-	<0.02 - 4.68	<0.032 - 0.98	<0.02 - 0.67
Hg	-	-	-	<0.082 - <0.250	<0.1 - <0.19
K	70 - 3,360	-	-	33 - 215	5.68 - 358
Li	0.2 - 87	-	-	0.053 - 1.97	0.058 - 1.70
Mg	0.5 - 265	-	<0.4 - 37	0.235 - 18.2	0.004 - 129.8
Mn	-	-	<0.02 - 0.13	<0.006 - 0.019	<0.004 - 0.021
Mo	-	0.9 - 8.8	<0.04 - 0.50	0.293 - 1.65	0.081 - 2.34
Na	370 - 14,400	-	33 - 600	40 - 308	24 - 1,137
Ni	-	-	-	<0.002 - 0.080	0.014 - 0.066
Pb	-	-	<0.0005 - 0.009	<0.042 - 0.41	<0.03 - 0.41
S_2O_3	-	0 - 260	-	-	-
Sb	-	-	<0.002 - <0.003	-	-
Se	-	0.02 - 0.15	<0.001 - 0.05	<0.002 - 0.010	<0.004 - 0.075
Si	5.4 - 122	-	-	5.4 - 46.2	1.2 - 63.8
Sn	-	-	-	<0.060 - 0.30	<0.04 - 0.13
SO_4	-	990 - 6,530	-	-	-
Sr	0.7 - 10.8	-	-	0.080 - 4.72	0.023 - 5.68
Tl	-	-	-	<0.054 - <0.062	<0.06 - <0.14
Ti	-	-	-	<0.008 - 0.034	<0.002 - 0.058
W	-	-	-	<0.048 - 0.99	<0.007 - 0.82
V	-	-	<0.10 - 2.63	0.095 - 1.90	0.017 - 1.70
Zn	<0.01 - 0.48	-	<0.003 - 0.143	<0.5 - <0.8	<0.01
pH	7.75 - 10.6	7.8 - 9.0	8.3 - 10.7	8.78 - 11.60	8.89 - 11.70
Type of Study	Column	Column	Shaker	Shaker	Shaker
Particle Diameter	-100 mesh	-100 mesh	-100 mesh	-100 mesh	-100 mesh
Solid-to-Liquid Ratio	-	-	0.2 g/mL	0.2 g/mL	0.2 g/mL
Contact Time	24 hrs.	31 days	48 hrs.	48 hrs.	48 hrs.
Column Description	0.7 x 15 cm glass columns	1.5 x 15 cm plastic columns	-	-	-
Pore Volumes	0.28 - 1.11	1	-	-	-



Zone 1 -- Black carbonized shale, thin bedded, fissile.
Zone 2 -- Same as Zone 1, except light gray to tan and brown in color, soft.
Zone 3 -- Light gray to tan, very soft, "frothy" appearance due to presence of coalescing vugs, bedding and fissibility substantially gone.
Zone 4 -- Variegated greens, black, gray, brown, yellow; highly porous; fused; clinker-like material, hard; not friable; remnant bedding present but not pronounced.
Zone 5 -- Buff-tan, very soft, similar to Zone 3 except vugs absent.

Figure 5-5. Schematic diagram of zones of spent shale in a vertical cross section of the Geokinetics Retort 1 (Leenheer and Stuber, 1977).

The chemical composition of leachates from Retort 1 and the Cleave et al. (1979) samples are summarized in Table 5-6. The ranges correspond to the different zones. The mineralogical controls responsible for these concentrations will be discussed in the section on leaching mechanisms. The range in values is due to different mineral phases present in each zone.

TABLE 5-6

Inorganic Composition of Leachates From Geokinetics Spent Shale (mg/L).

	Cleave et al., 1979	Krause et al., 1980	Krause, et al., 1980
As	-	0.01 - 0.2	0.03 - 0.3
B	-	0.5 - 6.7	0.6 - 2.6
Ca	747	-	-
Cl	29	-	-
EC, µmho/cm	-	321 - 16,200	741 - 8,430
F	-	0.32 - 10.1	2.3 - 13
HCO_3	797	-	-
K	34.4	-	-
Mg	0.2	-	-
Mo	-	0.4 - 17.1	0.7 - 6.4
Na	542	-	-
Se	-	<0.001 - 1.3	0.006 - 0.16
SO_4	2,298	170 - 16,435	790 - 5,595
pH	-	8.8 - 11.6	9.2 - 11.6
Type of Study	Shaker	Column	Ball Mill/Batch
Particle Diameter	-	-1 in.	-10 mesh
Solid-to-Liquid Ratio (g/mL)	0.5	-	0.4
Contact Time	48 hrs.	≃1 hr.	2 wks.
Other	-	3 x 50 cm glass column	-

These data reveal that Geokinetics leachates have a pH that ranges from 8.8 to 11.6, consistent with pHs reported for other spent shale leachates. The electrical conductivity ranges from 321 to 16,200 μmhos/cm, and the trace elements which occur at the highest concentrations (among those studied) are B, F, and Mo. The conductivity and pH results in Table 5-6 are consistent with other studies on these samples reported by Leenheer and Stuber (1977). These results are not unlike those previously reported for Occidental spent shale leachates and for surface spent shale leachates.

Organic Composition of In Situ Leachates

The characterization of organics in in situ leachates presents special problems. We are not aware of any studies that have investigated the organics in leachates from field samples, although work is in progress at Occidental's research laboratories (Stover, 1981). [Total organic carbon was measured in Occidental core 3E1 (U.S. DOE, 1980) but this sample is believed to have been contaminated by organics present in polymers used during drilling.] The only organic characterization data available was developed using simulated spent shales from early runs of the LLNL retorts and the LETC 10-ton retort. We will summarize that data here as an indicator of organic quality of in situ leachates.

The leaching of organics from simulated in situ spent shales has been investigated by Amy (1978), Amy and Thomas (1977), and Hall (1982). Amy studied samples from four early runs of LLNL's small, 125-kg simulated in situ retort, and Hall studied samples from one run of LETC's 10-ton retort. Important characteristics of these runs are summarized in Table 5-7. None of these runs are similar to conditions expected in in situ retorts. The two inert gas runs studied by Amy are more similar to indirect-heated surface processes (Table 2-1) than they are to in situ processes. They are presented here for comparative purposes. The three combustion runs also differ from in situ processes as they exist today. The maximum retorting temperature of Amy's type 1 and of Hall's samples is low. The retorting rates are fast, and the sweep gas compositions are different from those proposed for a commercial facility.

Amy evaluated the effect of several variables, including leach water temperature, leach water quality, and particle size, on the total amount of organic carbon that is solubilized from spent shale. These studies revealed that in 30 days, from 1.0 to 12 mg of total organic carbon may be leached per 100 grams of in situ spent shale at water temperatures of 20 C to 80 C (Table 5-8). The details of these mechanistic studies will be summarized in another section.

Amy also conducted preliminary studies to characterize the organics in his leachates. He separated his samples into acidic, basic, and neutral fractions using a hexane solvent system and pH adjustment. He also measured phenols and organic nitrogen. The results of these analyses are summarized in Table 5-9.

TABLE 5-7

Retorting Characteristics of Simulated In Situ Spent Shale Samples Studied by Amy (1978) and by Hall (1982).

Sample	Type of Run	Maximum Temperature (C)	Sweep Gas	Retorting Rate (m/day)	Retort
Amy, 1978 Type 1	Combustion	750	air/N_2 (7.6% O_2)	0.69	LLL 125-kg
Amy, 1978 Type 2	Inert Gas	510	N_2	1.40	LLL 125-kg
Amy, 1978 Type 3	Combustion	935	air/recycle (10.5% O_2)	1.34	LLL 125-kg
Amy, 1978 Type 4	Inert Gas	460 - 530	N_2	∿ 2	LLL 125-kg
Hall, 1982	Combustion	650	67% air/33% steam	0.93	LETC 10-ton

Amy's fractionation data indicate that about equal quantities of acidic, basic, and neutral materials are present in most leachates and that the neutral fraction is predominant in leachates from inert gas spent shales. The concentration of phenols ranged from 0.23 to 0.41 mg/L and of organic nitrogen, from 0.4 to 1.4 mg/L. The relatively high phenolic concentrations (1 μg/L has been recommended for domestic water supplies and to protect against fish flesh tainting (U.S. EPA, 1976; NAS, 1973)) could create aesthetic, odor, and taste problems in drinking water supplies and requires additional study. The phenol concentration is lower in the combustion run than in the inert gas run leachates while there is no significant difference among the various runs for organic nitrogen. The phenol and organic nitrogen together constitute about 6% to 9% of the total organic carbon (Table 5-8) while the organic nitrogen constitutes about 7% to 39% of the base fraction.

Hall (1982) analyzed a hexane extract of a composite leachate sample from a large column experiment using gas chromatography-mass spectrometry (Finnigan Model 4023; 30m OV-101 capillary column). Phenols were determined as the methyl-phenyl ether using perdeutero phenol as an internal standard. The results of his analyses are presented in Table 5-10. Only a few phenols and pyridines at the parts-per-billion level were found. This represents about 0.25% of the total organic carbon present in the sample (TOC = 6.6 mg/L).

This represents the first time known to the authors that alkyl pyridines have been identified in any oil shale leachate. Riley et al. (1981) looked for alkyl pyridines in Paraho leachates, but they were below his detection limit. This is potentially significant because these water-soluble compounds are known to be persistent and mobile in the geohydrologic system of oil shale regions (Riley et al., 1981).

TABLE 5-8

Quantities of TOC Leached From Simulated In-Situ Spent Shale (Amy, 1978).

Experiment	Particle size range, cm	Water	Leaching time	Inert gas retorting[a]	Combustion retorting[b]	Combustion and recycle gas retorting[c]
30-day batch, 20 C (Amy, 1978)	0.06 - 0.3	Distilled	30 days	1.5 - 2.2	1.0 - 1.6	3.5
30-day batch, 80 C (Amy, 1978)	0.06 - 0.3	Distilled	30 days	2.2 - 6.0	1.0 - 2.0	2.9
30-day batch, 20 C (Amy, 1978)	0.06 - 0.3	Synthetic ground[d]	30 days	1.5 - 2.7	1.0 - 1.4	3.8
30-day batch, 80 C (Amy, 1978)	0.06 - 0.3	Synthetic ground[d]	30 days	4.0 - 6.8	1.0 - 1.8	3.4
Continuous-flow column (Amy, 1978)	0.06 - 0.03	Distilled	80 hr.	4.1 - 6.9[e]	3.8,4.4[e]	9.7,11.8[e]

[a] Range corresponds to four solid:water ratios ranging from 50 g shale/30 mL water to 50 g shale/200 mL water for one sample and 50 g of shale/50 mL water for a second, inert-run spent shale sample.

[b] Range corresponds to four solid:water ratios ranging from 50 g shale/30 mL water to 50 g shale/200 mL water for a single combustion run spent shale.

[c] Sample value for one combustion-recycle spent shale leached using 50 mL water per 50 g of shale.

[d] Synthetic groundwater had a conductivity of 12,000 μmho/cm and a pH of 9.

[e] TOC leached after 80 hr. in, respectively, a 12-in-long and a 6-in-long column. Two unique samples were tested in each column for the inert run and one sample was used for the combustion and combustion-recycle runs (see Table 5-7).

TABLE 5-9

Acid, Base, and Neutral Fractions and Phenol and Organic Nitrogen Content of Simulated In-Situ Leachates (μg/100g) (Amy, 1978).

Water	Experiment	Constituent	Inert Gas		Combustion	Combustion/ Recycle
			Type 2	Type 4	Type 1	Type 3
Distilled	Batch, 20 C	Acid	370	880	680	360
		Base	510	540	460	290
		Neutral	880	1050	860	280
		Total Fractions	1760	2470	2000	930
		Organic N	70	100	70	90
		Phenol	43	41	25	22
	Batch, 80 C	Acid	450	720	500	330
		Base	330	360	610	470
		Neutral	350	890	180	520
		Total Fractions	1130	1970	1290	1320
		Organic N	70	140	40	130
		Phenol	30	35	23	15
Synthetic Groundwater	Batch, 20 C	Acid	920	-	420	-
		Base	440	-	370	-
		Neutral	1600	-	660	-
		Total Fractions	2960	-	1450	-
		Organic N	90	90	90	70
		Phenol	-	-	-	-
	Batch, 80 C	Acid	1100	-	500	-
		Base	590	-	330	-
		Neutral	2300	-	360	-
		Total Fractions	3990	-	1190	-
		Organic N	90	120	70	60
		Phenol	-	-	-	-

TABLE 5-10

Organic Compounds Identified by GC-MS in Simulated In Situ Spent Shale Leachates From a Steam/Air Run of LETC's 10-ton Retort. [Sample was taken 30 days after the run was complete. The column was not emptied, and the leachate remained in contact with the shale over this period (Hall, 1982)].

Compound	Concentration (ppb)
Phenol[a]	5.4
o-cresol	3.1
p-cresol	1.6
dimethyl phenol	1.6
methyl-ethyl phenol	0.7
trimethyl pyridine[b]	2.0
dimethyl-ethyl pyridine	1.1
dimethyl-ethyl pyridine	0.5
alkyl pyridine (unidentified)	0.3

[a] Phenols determined as the methyl-phenyl ethers using perdeutero phenol as an internal standard.

[b] In polysubstituted alkyl compounds, the mass spectrum was not intense enough to positively identify the position isomers of the alkyl groups.

These results suggest that the organics in in situ leachates are a complex mixture of compounds which individually are present at relatively low concentrations, the majority of which are nonvolatile. The high concentration of phenolics (and perhaps other compounds) suggests that additional study of the organics is warranted.

IN SITU SPENT SHALE LEACHING MECHANISMS

The formation and transport of in situ spent shale leachates have been approached from both an experimental and theoretical standpoint. Some investigators have or are developing computer models of water and solute transport in abandoned in situ retorts (Brown et al., 1977; Hall, 1982; Fitzpatrick, 1982; Robson and Saulnier, 1981; Mehran et al., 1980). Most investigators, however, have studied these phenomena using experimental techniques, laboratory and field studies designed to measure the composition of leachates for a given set of conditions (Peterson et al., 1981; Krause et al., 1980; Jackson et al., 1975; Stollenwerk, 1980; U.S. DOE, 1980, etc.).

This section will address the formation and transport of leachate within an in situ retort. We will overview the theoretical framework of water and solute transport followed by a discussion on laboratory studies that address the mechanisms of in situ leachate formation. A subsequent section will address the transport of leachate away from an in situ retort. Aquifer transport is treated separately because the chemical and physical dimensions of the problems are different.

Modeling Studies

In situ spent shale will be leached by groundwaters following site abandonment as shown in Figure 1-2. Conceptually, the formation and movement of leachate through an in situ retort is analogous to the formation and movement of percolation through a surface spent shale disposal pile. It entails the movement of water and solutes through a porous medium. Although the problems differ in their physical (geometry, hydraulic properties of porous media, etc.) and chemical (spent shale mineralogy, chemical composition of leaching fluid) dimensions, the same theoretical framework applies to both.

The theoretical framework governing water and solute transport through a spent shale disposal pile has been previously reviewed (see page 4-49). The same underlying physics and chemistry, expressed by Eqs. (2-3) and (2-4), apply to in situ leachate formation and transport and, thus, will not be repeated here.

Water Movement

Modeling of in situ leachate formation and transport requires information or flow fields within the retort. The application of the conservation of mass equation to water movement through a porous medium is routine, and a large number of numerical methods have been developed to solve the resulting set of differential equations. Indeed, three investigators have used this approach to model water movement through an abandoned in situ retort (Brown et al., 1977; Mehran et al., 1980, 1981; Robson and Saulnier, 1981). All of these studies (and any future work) were limited by the availability of adequate laboratory and field data.

Modeling water movement through an abandoned in situ retort requires the accurate specification of the dependence of hydraulic conductivity on pressure head and of the initial and boundary conditions at the on-set of leaching. Thermal effects also may be important. These factors are difficult to specify with certainty for in situ retorts.

Water reinvasion into an in situ retort requires the treatment of unsaturated flow. This requires laboratory measurements of the relationship between pressure head and degree of saturation and hydraulic conductivity. Both of these properties are strong functions of particle size and distribution. This type of information is not available for in situ spent shale. Modeling studies have either assumed flow to take place in a fully water-saturated medium or the necessary relationships have been estimated. Neither is a satisfactory approach. And determining initial and boundary conditions requires detailed hydrologic modeling of surrounding aquifers from the initiation of dewatering through the completion of retort filling. This requires modeling of water movement in fractured media which is not feasible at the present due both to the absence of suitable numerical techniques and field data on fracture systems.

The most realistic simulation of the reinvasion process and of water movement through an in situ retort was done by Mehran et al. (1980). In that work, the equation of conservation of mass combined with Darcy's Law (Narasimhan and Witherspoon, 1977) was used to study groundwater reinvasion at Tract C-b. The results, summarized in Figure 5-6, indicate that initial reinvasion takes place primarily in the vicinity of the periphery of the retorted region because of high conductivity of that region. The water table gradually rises along the bottom length of the retorted region, starting with the upper surface of the lower aquifer. This behavior prevents the invasion of water into the upper aquifer for decades and perhaps centuries. Obviously, the reinvasion rate will vary from place to place, depending on the nature of saturation and other hydraulic properties of the medium. Mehran's results show that the average rise of the phreatic surface along the vertical section of the periphery of the retorted region is approximately 1.77 ft/yr.

The profiles of the phreatic surface after 200 years show that the upper aquifer remains essentially unaffected by the invading waters (Figure 5-6). This could have favorable environmental consequences by allowing sufficient time for control technologies to be implemented. Due to the high porosity and high hydraulic conductivity of the retorted region, it will act as a powerful sink to concentrate flow paths. Therefore, one should expect the reinvasion process to be extremely slow due to the large volume of void spaces that have to be filled and the extremely low hydraulic conductivity due to very low saturation and hysteresis effects. Thus, leaching reactions, discussed in a subsequent section, will reach equilibrium in the field.

Solute Transport

The transport of chemical species during the reinvasion process is governed by diffusion-convection phenomena in the unsaturated state, and, therefore, is an extremely complex problem. The conceptual framework of solute transport was discussed previously for surface spent shale percolation and the governing equation was presented as Eq. (2-4). As noted in that discussion, solute transport can be modeled by using either a "mass-transfer" or a "geochemical" approach. The mass transfer approach has been used by Amy (1978) and by Hall (1982) to describe the leaching of total organic carbon (TOC) from in situ spent shales while the geochemical approach is being investigated by DRI (Fitzpatrick, 1982) and by LASL (Peterson, 1981). The only published work on solute transport from in situ spent shale is that by Amy (1978) and Hall (1982) which will be overviewed here.

The work of Amy (1978) and of Hall (1982) assumed that the leaching and transport of solutes within the pores of a fixed bed of in situ spent shale could be described by the classic advection-dispersion equation:

$$\frac{\partial c}{\partial t} = E\frac{\partial^2 C}{\partial Z^2} - U_P\frac{\partial C}{\partial Z} - R\gamma - \frac{1}{m}\frac{\partial q}{\partial t} \tag{5-1}$$

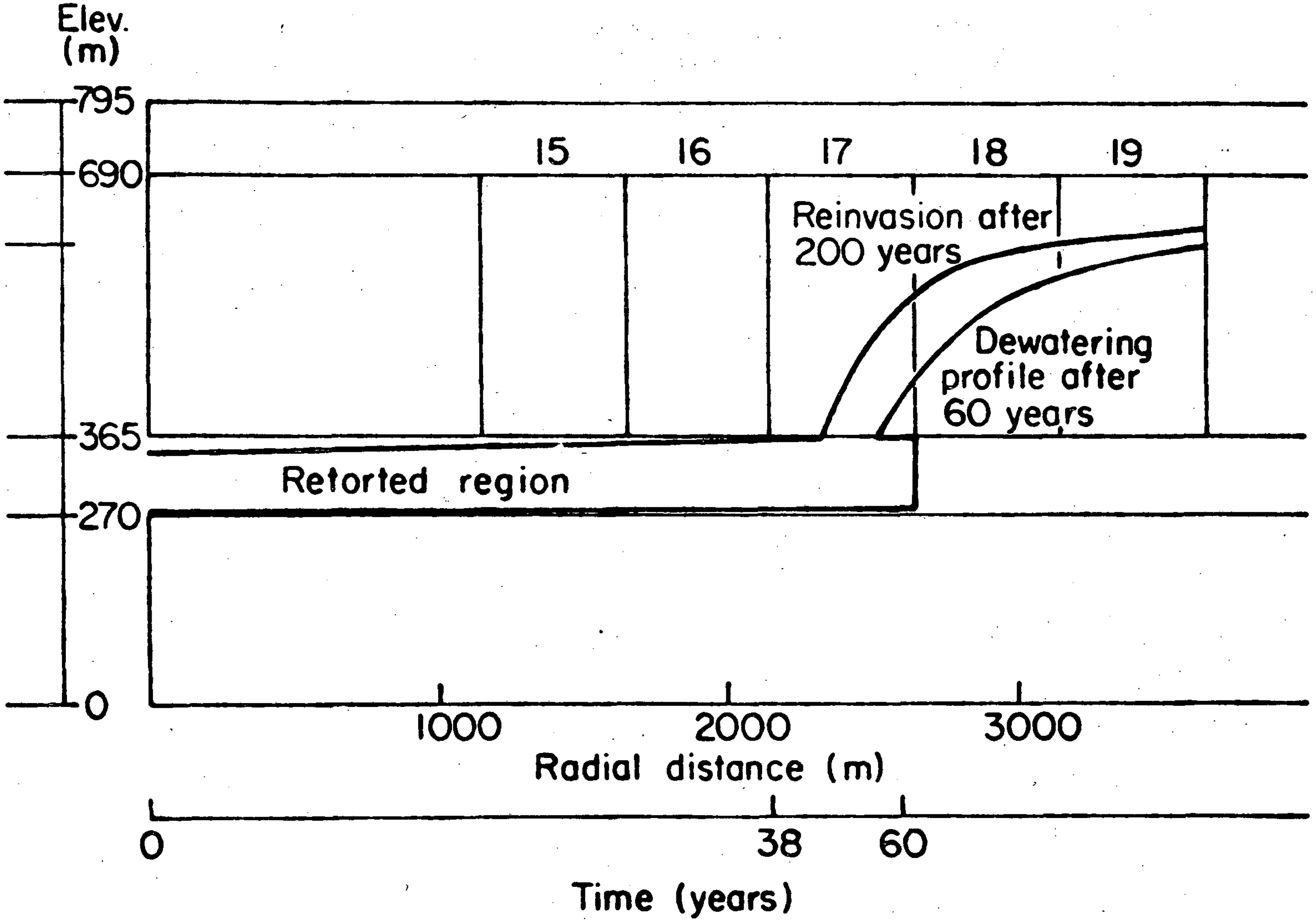


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Figure 5-6. Profile of phreatic surface after 200 years of reinvasion at C-b tract (Mehran et al., 1980).

in which:

C = Concentration of solute in liquid phase
t = Time
Z = Distance in direction of flow
E = Dispersion coefficient
U_p = Pore velocity
R_γ = Chemical reaction rate
m = Ratio of macro-pore to micro-pore volumes
q = Concentration of solute in solid phase

The terms on the right side of the equation represent dispersive transport, convective transport, chemical reaction, and internal mass transfer. A source term may be added, if necessary, and Equation 5-1 can be coupled with Fick's law of diffusion:

$$\frac{\partial q}{\partial t} = D_m \nabla^2 q \qquad (5\text{-}2)$$

in which D_m is the diffusion coefficient and ∇^2 is the Laplacian operator.

Amy (1978) and Hall (1982) both used batch and column tests in which simulated in situ spent shales were employed (see Table 5-7) to determine the various constants and numerical relationships necessary to apply Eq. 5-1 to the in situ leaching problem. Amy's model, which neglected the dispersive and reactive terms in Eq. 5-1, assumed that the leaching of TOC from spent shale could be expressed by mass transfer equations. Amy proposed the following equation:

$$\left(\frac{\partial q}{\partial t}\right)_Z = \frac{F}{\rho_B A}\left(\frac{\partial C}{\partial Z}\right)_t + \frac{1}{\rho_B}\left(\frac{\partial C}{\partial t}\right)_Z \qquad (5\text{-}3)$$

together with these mass transfer relationships:

<u>External Mass Transfer</u>

$$\left(\frac{\partial q}{\partial t}\right)_Z = K_E\,(C - C^*) \qquad (5\text{-}4)$$

<u>Surface Reaction</u>

$$\left(\frac{\partial q}{\partial t}\right)_Z = K_{BA}\,(q_\infty - q) \qquad (5\text{-}5)$$

<u>Internal Mass Transfer</u>

$$\left(\frac{\partial q}{\partial t}\right)_Z = K_G\,(q^* - q) \qquad (5\text{-}6)$$

where:

K_E = External mass transfer coefficient

C^* = Equilibrium leachate TOC concentration

C = Measured leachate TOC concentration

K_{BA} = Surface reaction rate coefficient

q_∞ = Maximum potential of solid phase TOC on shale surface

q = Actual solid-phase TOC on shale particles

K_G = Internal mass transfer rate coefficient

q^* = Equilibrium solid phase TOC concentration

t = Time

ρ_B = Bulk density of shale

Z = Distance in the direction of flow

F = Water flow rate

A = Cross-sectional area of column

Equation 5-3 was solved wth each of Eqs. (5-4), (5-5), and (5-6) to determine which mechanism was limiting for a given spent shale.

Amy found that internal mass transfer was rate limiting for type 1 (combustion) spent shale and that none of these models accurately described the rate of leaching over the entire range of time for type 2 spent shale (inert) (see Table 5-7).

Hall (1982) expanded upon Amy's work, developing a model based on Eq. (5-1) which used separate mathematical expressions to describe different leaching stages (rather than using a single mass transfer expression for a given spent shale). Hall formulated the leaching phenomenon as consisting of three separate stages, shown schematically in Figure 5-7. Stage I solute transport begins immediately upon introduction of water into a dry bed of spent shale. Soluble material moves from the surface of the solid to the liquid until phase equilibria is reached. Stage II mechanisms remove from the micropores the solute present at the time of the first pore volume passage of leachate. As soon as the concentration in the micropores drops, additional material is transported from the solid phase to the liquid in the micropores. The removal of this solute is accomplished by Stage III mechanisms. The depletion of soluble material at the particle surface forces solute to move to the phase interface from sites within the mineral matrix. After the Stage II solute has been removed, the transport of Stage III solute approaches steady state. Stage II and Stage III solute are thus present in the micropores at the same time.

Hall developed, solved, and verified mathematical models for the Stage II and III leaching mechanisms. No model was developed for Stage I. The mass transport equation for the Stage II model is given by:

$$\frac{C(X,T)}{C_o} = 1 - U(X,T) \qquad (5\text{-}7)$$

where:

$$C(X,\theta) = q_o + (C_{in}-q_o)\ \mathcal{L}^{-1}\left\{\frac{1}{s}\exp\left[-\alpha X\sum_{1}^{\infty}\left(\frac{s}{s+D_m\alpha_n{}^2}\right)\right]\right\}$$

$C(X,\theta)$ = Concentration in macropores at distance X and time θ

q_o = Concentration in micropores at time zero

C_{in} = Concentration in influent to bed

$\mathcal{L}^{-1}$ = Inverse of Laplace transform

s = Transform variable

α = $4\ D_m\ /\ b^2$

D_m = Diffusion coefficient

α_n = Roots of $J_o\ (b,\alpha_n) = 0$, in which J_o is a Bessel function of zero order

and

$$U(X,T) = \mathcal{L}^{-1}\left\{\frac{1}{s}\exp\left[-\alpha X\sum_{1}^{\infty}\left(\frac{s}{s+[0_i]^2}\right)\right]\right\}$$

$[0_i]$ = Zeros of the Bessel function of the first order

T = $D_m\ \theta/b^2$

The mass transport equation for the Stage III model is given by:

$$\frac{dC}{dt} = \frac{1000}{\varepsilon}\ K_o(C_e-C) \qquad (5\text{-}8)$$

where

K_o = Mass transfer coefficient

a = Interfacial area

C_e = Equilibrium concentration in liquid phase in contact with solid phase

C = Liquid phase concentration

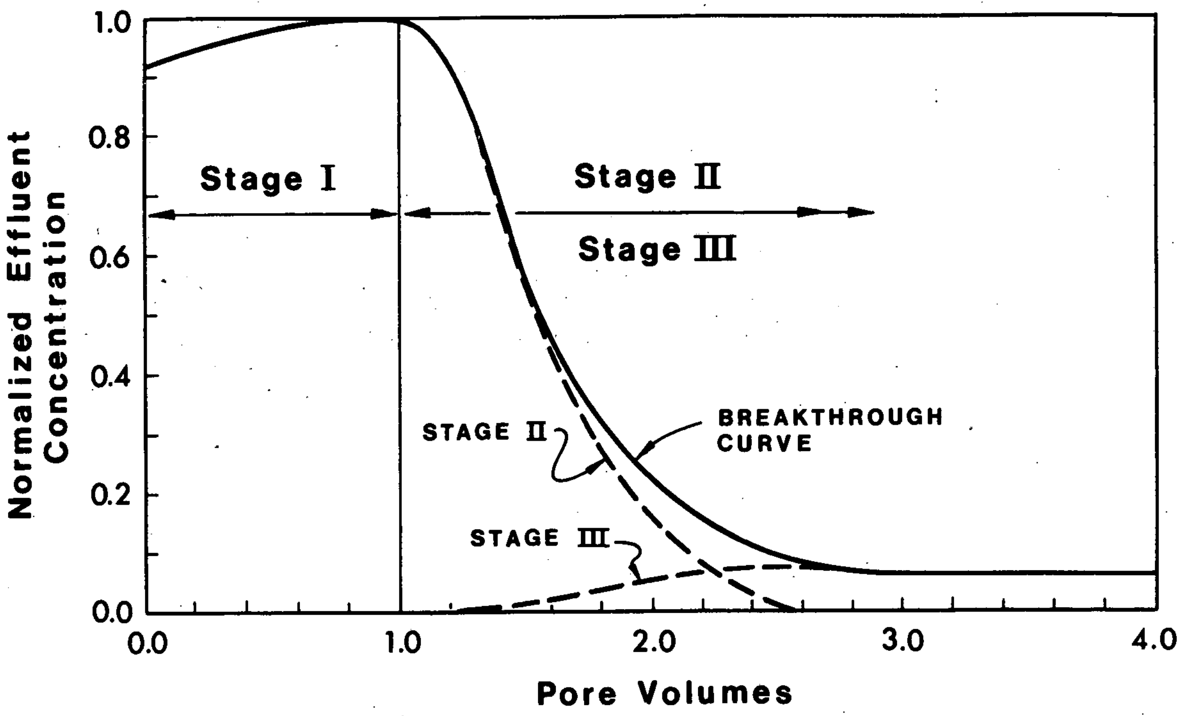

Figure 5-7. Schematic column breakthrough curve showing contributions of various mechanisms (Hall, 1982).

This same mathematical model also is applicable to surface spent shales and to other constituents whose leachate concentrations are governed by mass transfer phenomena. It is important to note the relevance of this type of fundamental approach in studying leaching. Most leaching studies have focused on detailed chemical characterizations of spent shales and leachates without consideration of inter-and intra-particle mass transport or some other theoretical framework. These types of studies are little more than tabulations of chemical data, valid only for a given sample of spent shale and for a particular set of experimental conditions. Extrapolation of such results to other samples or conditions is impossible. Thus, this latter type of "characterization" study is discouraged in the future.

Experimental Studies

Most leachate investigations have used laboratory techniques, in the absence of a modeling or other theoretical framework, to measure leachate composition for a given set of conditions. These studies, rather than developing "characterization" data per se, have taken a mechanistic approach, focusing on variables that control the composition of leachates. Unfortunately, the vast majority of this work has focused on chemical characterization of leachates for a limited range of leaching variables (i.e., solid-to-liquid ratio, contact time, particle size) and ignored raw shale and spent shale compositions. Therefore, much of the resulting data is relevant only for a specific sample and a specific set of experimental conditions. This is also true of surface spent shale leaching studies, discussed previously. This section represents an attempt to organize in situ spent shale leaching data into a consistent theoretical framework.

The leaching of inorganic and organic material from in situ spent shales is a complex physico-chemical process which depends on the mineralogical, chemical, and physical characteristics of the spent shale and on the quality, temperature, and flow regime of groundwater migrating through an abandoned retort. The characteristics of the spent shale, in turn, depend on both the mineralogy of the original raw shale and on the processing conditions that it experienced during oil extraction. The total number of variables that ultimately affect the concentration of a constituent in leachates is large and includes the following:

- raw shale mineralogy
- retorting temperature
- time at temperature
- inlet gas composition
- particle size and void distribution in spent shale bed
- groundwater quality and temperature
- groundwater flow velocity
- surface chemistry of spent shale
- temperature of spent shale
- microbial activity.

Each one of these variables depends on a large number of other factors. About 20 separate mineral phases have been identified in in situ spent shale. Sweep gases may contain half a dozen chemical species at the fractional volume percentage level. Groundwaters may contain several dozen ions at the part-per-million level, and so on.

The in situ leaching process is very complex, and a complete understanding of it requires a systems approach that follows a raw shale of known mineralogy through retorting, retort abandonment, and leaching. Important variables must be determined, reasonable variable ranges should be established from a knowledge of the technology, and the variables should be accurately measured and recorded.

Unfortunately, this approach has not been followed in in situ (or surface) leaching research to date, although LANL has adapted it (Peterson et al., (1982). Most studies have focused on one or more isolated aspects of this complex process, and sufficient information has not been provided to allow comparisons among the studies and general assessments of in situ leaching. Raw shales of varying mineral composition (Colony Mine, Anvil Points, Logan Wash) have been retorted under a wide range of conditions, and the spent shales leached under many different conditions. The results of these studies have singularly or collectively been used to assess and characterize "in situ" spent shale leachates. This has led to many erroneous conclusions.

This section will attempt to put the mechanisms of in situ leaching into perspective. The information available will be organized by variables, and the relevance of each study to in situ leaching will be addressed. The reader is reminded that the <u>definitive</u> leaching experiment that would allow prediction of environmental impacts has not been conducted. The work that has been done has contributed to our understanding of fundamental processes and indicates "trends". However, a reasonable simulation of in situ leaching has not been achieved in the laboratory.

Retorting Conditions

The chemical quality of leachates depends on primary (desorption, dissolution) and secondary (precipitation, ion exchange, adsorption, diffusion, dispersion) rock-water interactions. The retorting process affects the degree to which these types of interactions will occur. Several investigators have demonstrated that retorting temperature, time at temperature, and atmosphere exert an important influence on leachate composition.

This section will review those studies that have employed small laboratory reactors to investigate the effect of retorting conditions on leachate composition. The results of these studies typically have not been related to spent shale mineralogy and in many cases, spent shale mineralogy was not determined. Thus, we will attempt to interpret some of these data using the mineralogical reactions information presented in a previous section. This discussion will be followed, in the next section on "Physical and Chemical Mechanisms," by a discussion of the relationship between spent shale mineralogy and leachate composition, based on laboratory leaching studies of cores from field retorts. In that case, the retorting conditions are unknown, and the investigators attempted to infer retorting conditions from spent shale mineralogy and leachate composition. The authors are aware that this is an awkward development, but the available data do not lend themselves to a more cogent treatment at the present. Ideally, the next two sections should be treated together, developing first the relationship between retorting and spent shale mineralogy and then, the relationship between that mineralogy and leachate composition. Instead, the relationship between retorting conditions and leachate composition, inferring underlying mineralogy, is discussed first. Then the relationship between spent shale mineralogy and leachate composition, inferring retorting conditions, is discussed.

The relationship between retorting conditions and spent shale mineralogy is well established and has been studied by many investigators, as discussed previously. The principal conclusion from that work is that in situ spent shales will consist of a complex mixture of silicates. The solubility of the resulting mineral phases and secondary, aqueous-phase solubility controls probably are the major factors that regulate leachate quality (Peterson et al., 1982).

Several investigators (Bethea et al., 1981; Peterson et al., 1982; Park et al., 1980) have studied leachability as a function of retorting conditions. Park et al. (1980) studied the solubility of major ions as a function of maximum retorting temperature. Logan Wash raw shale was retorted in 100 C intervals (500-1200 C) for 23 to 89 days in air. The spent shale was ground to -325 mesh, batch leached for one hour (0.05 g/mL), and the leachates were analyzed for Na, Ca, Mg, Si, SO_4, K, and pH (Figure 5-8). The mineralogy for these samples was presented in Figure 5-3. This retorting regime is believed to simulate the Occidental VMIS process. Steam, anticipated for use as a sweep gas, would tend to accelerate the solid-solid mineral reactions and shift the mineral and leachate minima and maxima to lower temperatures (Figure 5-4).

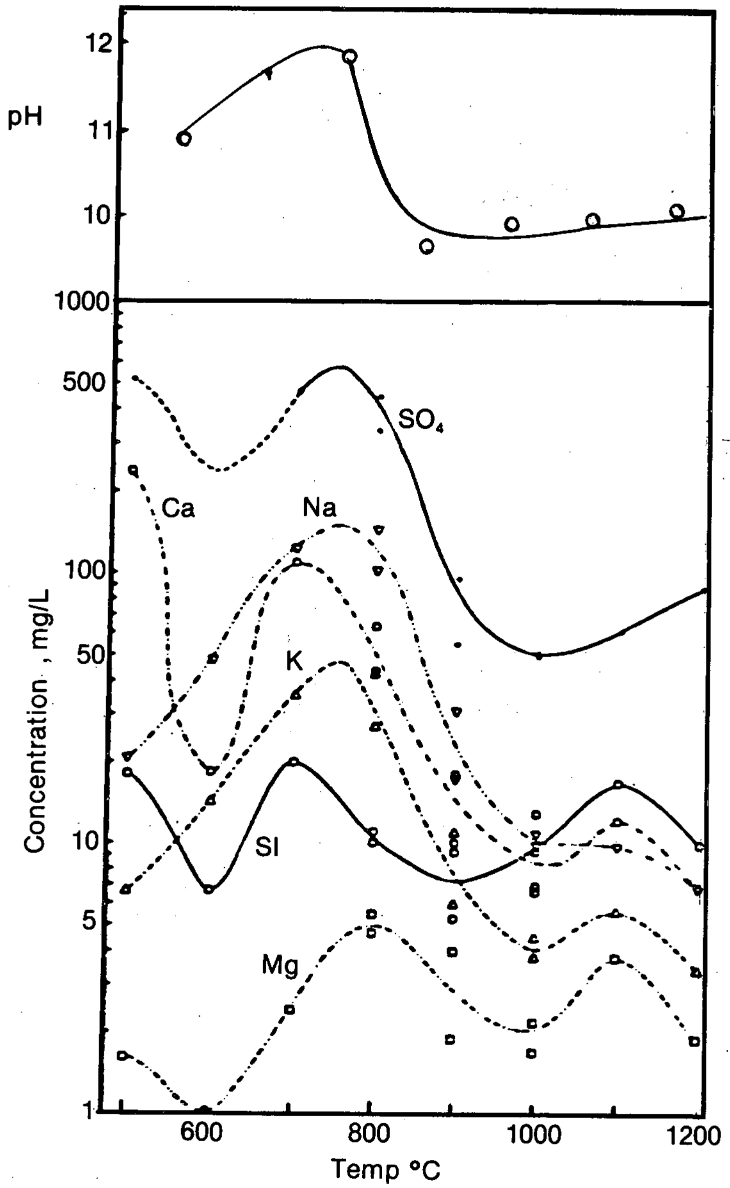

Figure 5-8. pH and concentration of dissolved ions in leachates from spent shale pellets retorted for up to 23 to 89 days in air. Pellets were batch leached with deionized water for 1 hr at a 0.05 g/mL solid-liquid ratio. Particle size was -325 mesh. (These are the same samples as represented in Figure 5-3, Modified from Park et al., 1980).

This study demonstrated that the concentration of these constituents decreases at the high temperatures expected in in situ retorts, compared to lower temperatures, and that maximum retorting temperature exerts a significant influence on leachate quality. As retorting temperature increases from 800 C to 1200 C (the range expected in commercial VMIS retorts), the concentrations of Na, K, Ca, and SO_4 in the leachate decrease approximately ten-fold.

An examination of Park's data indicates that all of the elements studied go through maxima at around 700 to 800 C and again around 1100 C. The first maxima occurs at the same temperature at which both forsterite and akermanite reach maxima. Since forsterite is insoluble (Dean, 1979), either akermanite is relatively soluble, or another mineral phase controls the concentration of these ions. Peterson et al. (1982) also noted that trace elements show increased mobility from samples in which akermanite is the major mineral phase. This suggests that VMIS retorts will have to be operated to minimize this mineral phase if leachate concentrations are to be held to low levels. The second maxima in leachate concentrations is about an order of magnitude lower than the first for Na, Ca, and K and is probably controlled by an unknown mineral phase since diopside, which is the major mineral around 1000 C, is insoluble.

All of the ions (SO_4, Ca, Si, Mg) except Na and K have minima at 600 C and 1000 C. Mineral studies (Figure 5-3) indicate that periclase, which is insoluble (Dean, 1979), peaks at 600 C and that the more soluble carbonates, dolomite and calcite, occur at quite low levels around 600 C. The second minima coincides with the peak in diopside concentration. These results are consistent with mineral solubility data (Dean, 1979). Sodium and K, which do not have minima at 600 C, may be controlled by the feldspars or some other mineral phase.

Peterson et al. (1982), in related work, studied the effect of maximum temperature and retorting atmosphere on leachate composition (Figure 5-9). Colony Mine raw shale was retorted in air, N_2, and CO_2 in 200 C intervals (673 - 1073 C) for six hours. The spent shales were ground to -100 mesh, batch leached for 48 hours (0.2 g/mL), and the leachate analyzed for 30 constituents. Mineralogical analyses are in progress and were not available when this report was written. Note that this work is not comparable to that of Park et al. (1980). Peterson's retorting experiments used a relatively short time at maximum temperature (6 hours compared to 23 days or longer). Figure 4-3 indicates that this will result in important differences in mineralogy (and, therefore, in leachate composition). Peterson's conditions are more comparable to the Geokinetics process, especially the air runs, than they are to the Occidental VMIS process. The particle sizes and solid-to-liquid ratios also differed between these two studies.

Peterson's work generally agrees with Park's, although details differ due to mineralogical differences among the shales. The concentration of most elements decrease between 600 and 800 C, reaching relatively low levels at 1000 C. This is consistent with Park's results. Peterson compared the concentrations obtained at 1000 C with water quality criteria (U.S. EPA, 1976) and found that of the elements studied (As, Se, Ni, K, Na, Mg, Ba, Si, B, Al, Ca, W, Sr, and Ti), only Ba, V, Mo, Pb, and Li exceeded limits.

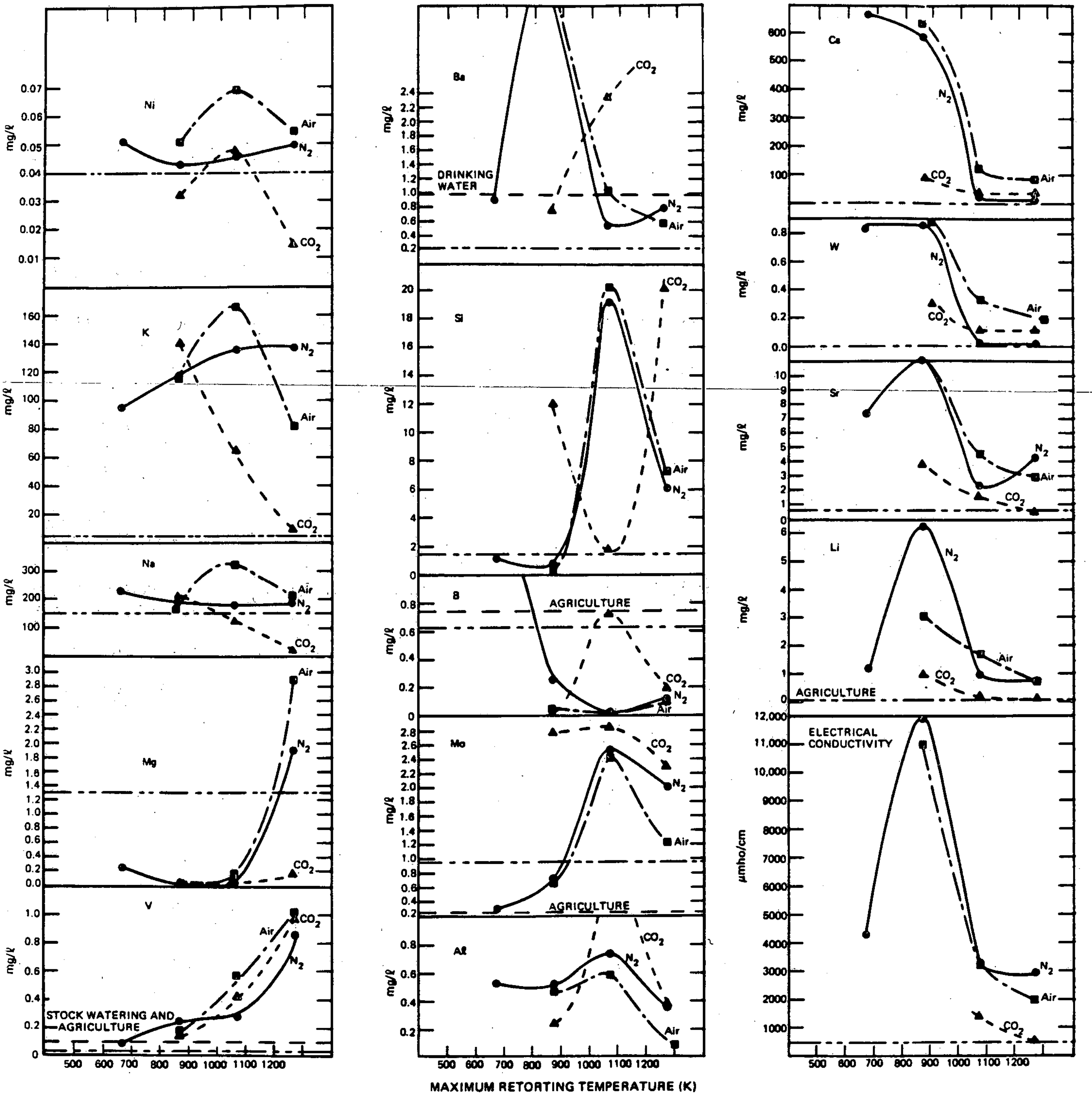

Figure 5-9. Effect of retorting temperature and atmosphere on the concentration of some trace element in laboratory-produced spent shale leachates. Legend for horizontal lines — -- — -- — raw shale leachate; --- water quality criterion. The Li water quality criterion for agricultural use coincides with raw shale leachate concentration (Peterson et al., 1982).

Although most constituents were lower in the leachates from higher temperature spent shales, certain other elements increased with temperature. Both Mg and V increased rapidly with temperature from 600 to 1000 C for air, N_2, and CO_2 atmospheres. The Mg result is different from that obtained by Park et al. (1980). Potassium and Ni increase slightly with temperature in N_2 atmospheres, and Ba and Si increase rapidly with temperature in CO_2 atmospheres. Thus, while the mobility of many elements decreases at high temperatures, these same conditions enhance the mobility of certain other elements. This may be due to changes in solubility of spent shale minerals or to the release of aqueous phase solubility controls.

Bethea et al. (1981) reported two studies on the effects of retorting temperature, time at temperature, and atmosphere on leachate composition. In the first, a Colorado raw shale (of unknown stratigraphy) was retorted in air (CO_2 was removed by bubbling the air through aqueous NaOH) and N_2 at 430 to 780 C for 15 or 30 hours. The spent shales (1 mm to 63 μm) were agitated for 15 hours (0.2 g/mL) and the leachates analyzed for the elements in Table 5-11. (Other elements were measured, but there was evidence of contamination, or most of the samples was below the detection limits.) The first set of experiments is not representative of in situ processes due to the low temperatures used. However, this study does provide information on variables not investigated by Park et al. (1980) and Peterson et al. (1982). Thus, while their studies are not directly applicable to in situ processes, they do provide additional mechanistic data that is important in developing a unified understanding of the in situ leaching process.

Many of the trends obvious in their data (Table 5-11) can be related to probable mineral phases present in the spent shale, as discussed in subsequent sections. For example, pHs of 11 to 12 present in all leachates from samples retorted at 780 C and 1000 C are probably due to the presence of lime in the spent shale. Similarly, the low concentration of Mg in leachates from 630 C and 780 C samples is probably due to the decomposition of dolomite (solubility is 0.032 g/100g) and the formation of MgO, which is insoluble. The reader is invited to identify other trends, based on probable mineral changes that occur at the various temperatures. The authors, however, will not analyze the data, and present it without further comment.

Bethea et al. (1981) investigated a different set of retorting variables in a second set of experiments employing actual groundwater. In this work, Utah shale from Hells Hole Canyon was retorted in air and in air plus 15% CO_2 at 430 C, 780 C, and 1000 C for 2 or 23 days. The spent shales (75μm to 4.75 μm) were batched leached (about 0.2 g/mL) using Douglas Creek and Bird's Nest Creek groundwater for 21 days and the leachates analyzed for the elements shown in Table 5-12. (Contamination was noted for Fe, Cr, Mn, and Cu.) This set of experiments is a reasonable simulation of field in situ leaching. However, the data are more difficult to interpret than Peterson's and Park's because an additional set of variables (leach water chemistry) was introduced. Thus, this work will be discussed in some detail in the section on water quality. In general, this study reveals that pH, EC, Na, Zn, and Mg decrease between 780 and 1000 C. Other constituents, including B, Ca, and K, increase over this same range. This disagrees with both Park et al. (1980) and Peterson et al. (1982) who found that Ca, Mg, and B decrease in this temperature range. This discrepancy is probably due to the chemistry of the new ions supplied by the groundwater and points to the problems of drawing conclusions from distilled water leaching data.

TABLE 5-11

The Effect of Some Retorting Variables on Leachate Quality (Bethea et al., 1981).

Retorting Temperature (°C)	Time at Temperature (hrs)	Leachate Concentration[a] (mg/L)							
		pH	TDS	Na	K	Ca	Mg	Sr	Li
		Retorted in the Presence of Air (0.25 L/min)							
430	15	7.76	888	348	24	966	80	14	1.85
	30	8.38	898	342	21	974	29	15	1.66
483	15	11.63	1063	222	26	1504	0.16	20	0.92
	30	12.02	1235	261	34	1573	0.13	24	1.26
630	15	12.33	1243	114	52	1481	0.08	47	0.98
	30	12.71	1725	154	76	2079	0.02	87	1.52
780	15	12.22	1688	640	157	752	0.08	24	3.90
	30	11.99	1458	770	185	680	0.08	15	4.18
		Retorted in the Absence of Air							
430	15	8.88	250	207	7.6	137	8.8	0.06	0.28
	30	9.73	178	128	9.4	59	6.1	0.04	0.20
483	15	10.55	215	122	8.6	92	0.9	0.10	0.60
	30	10.03	193	136	8.5	61	7.2	0.06	1.00
630	15	12.02	1775	102	13	796	0.4	28	3.33
	30	12.01	1948	88	12	781	0.4	22	4.48
780	15	12.02	-	426	29	886	0.4	19	8.14
	30	11.63	1110	214	23	437	0.3	6	3.76

[a] Solid-to-liquid ratio = 0.2 g/ml; contact time = 15 hrs; samples continuously agitated; leach water = distilled water; spent shale produced by laboratory retorting of Anvil Points, Colorado, oil shale; particle size = 1 mm to 63 μm.

TABLE 5-12

The Effect of Some Retorting and Leaching Variables on Leachate Composition (Bethea et al., 1981).

LC

Retorting Temperature (^oC)	Time at Temperature (days)	Leaching Temperature (^oC)	pH	Conductivity (μmhos/cm)	Leachate Concentration[a] (mg/L)									
					CO_3	HCO_3	Ca	Mg	Na	K	Ba	Zn	B	F
					Douglas Creek Groundwater (air only)									
Douglas Creek Water Quality			8.96	13.7	86	663	0.45	0.4	360	1.7	–	0.03	<0.01	4
430	2	35	8.55	4,300	413	415	601	200	480	42	5.0	0.24	1.78	26
		90	8.21	4,050	393	400	501	36	531	150	–	0.21	1.70	26
780	2	35	12.00	23,000	247	–	21.0	–	1481	426	2.5	0.06	1.75	39
		90	12.30	41,400	690	–	0.2	–	2841	2352	5.0	0.15	2.88	41
	23	35	11.86	13,950	178	–	1.2	–	1200	460	–	0.18	–	–
		90	11.96	19,900	343	–	0.5	–	2001	1323	–	0.18	–	–
1000	2	35	11.48	10,980	392	–	130	0.1	901	651	5.0	0.06	6.10	34
		90	11.44	12,680	433	–	0.5	–	801	1452	–	0.03	8.30	34
					Bird's Nest Creek Groundwater (air only)									
Bird's Nest Creek Water Quality			7.73	7,200	–	530	165	280	1060	11	–	0.18	1.9	3
430	2	35	8.67	8,480	344	345	179	250	1221	71	2.5	0.18	1.75	24
		90	8.22	7,500	344	350	551	44	1361	175	5.0	0.18	1.80	24
780	2	35	12.15	33,000	542	–	34	0.2	2481	751	–	0.12	2.15	38
	23	35	11.77	15,300	159	–	1.4	0.1	1921	4509	–	0.03	–	–
		90	12.00	23,300	287	–	0.4	–	3122	1652	–	0.08	–	–
1000	2	35	11.28	13,600	369	–	206	0.1	1622	700	–	0.09	9.2	26
		90	11.03	14,840	270	–	202	0.2	1481	2052	5.0	0.09	6.7	23

[a] Batch leaching for 21 days

Amy (1978) tried to relate the pH, conductivity, and total organic carbon of leachates from simulated in situ spent shales to retorting conditions (Table 5-7). His samples came from large pilot retorts operated to derive process information rather than leaching data. Thus, the effect of individual retorting variables could not be easily identified. However, Amy was able to conclude that the highest levels of organic carbon were associated with leachates from spent shales produced during inert-gas retorting or combustion retorting using recycle gas as a sweep gas. The inert-gas leachates also had the highest concentrations of phenols, and neutral compounds were the predominant fraction in inert-gas leachates. Amy also noted that different processing conditions altered the classes of organic compounds present in his leachates.

In summary, the studies of Park et al. (1980), Peterson et al. (1982), and Bethea et al. (1981) have demonstrated that temperature, time at temperature, and retorting atmosphere strongly affect the solubility of spent shales. This work also demonstrates that the concentration of many constituents in the leachates decrease by up to an order of magnitude between about 600 C and 1000 C, depending on retorting conditions. However, certain other elements increase in this same temperature range, refuting claims by Smith et al. (1978) that trace elements would be incorporated in the high-temperature silicates and become immobilized.

Physical and Chemical Mechanisms

As noted previously, the quality of leachates depends on desorption and dissolution of ions from the rock matrix and on subsequent precipitation, ion exchange, adsorption, diffusion, and dispersion reactions that occur between the hydrated species and rock materials. The various parameters of the retorting process (temperature, time at temperature, inlet gas composition, particle size, void distribution) will regulate the initial release of species from the spent shale. Characteristics of the aquifers (groundwater temperature and quality, flow velocity, media characteristics) will control the subsequent fate of leached constituents.

The initial concentration of ions in solution is affected by one or more of the following: solubility of a mineral phase in the spent shale (primary solubility), solubility of a mineral phase formed by precipitation from aqueous solution (secondary solubility), adsorption/desorption interactions between the spent shale and the leaching solution, and ion exchange equilibria. Identifying the specific reaction(s) which occur for any given ion or group of ions is a complex chemical problem which requires study of physico-chemical associations of the ion in the spent shale and the concentration and chemical form of the ion in the leachate.

Very little comprehensive work along these lines has been conducted on oil shale leachates. Several investigators have probed the mechanisms responsible for noted leachate composition by varying the particle size, liquid-to-solid ratio (R), equilibration time, and others. Unfortunately, the majority of this work has not been coupled with investigations of the mineral residence of the subject element nor with studies to speciate the element in the leachates and, thus, the results are largely inconclusive.

In this section, first a "conceptual" leaching framework will be developed from studies of Occidental (Peterson et al., 1982) and Geokinetics (Krause et al., 1980) core material. Both of these studies related spent shale mineral phases to observed leaching patterns. This discussion will focus on chemical controls in the immediate vicinity of a particle of spent shale. The reader should realize that this overview is based on preliminary leaching data and considerable additional work is required to confirm these tentative conclusions. Following this overview, the effect of important leaching [leachate water temperature, chemical quality and atmosphere, solid properties (particle size, surface charge), and experimental variables (solid-to-liquid ratio, contact time] on leachate composition will be explored.

Occidental. Peterson et al. (1982) have developed a conceptual framework for interpreting and understanding leachate chemistry. They studied the mineralogy and leaching behavior of 43 core sections from two coreholes from Occidental's Retort 3E. Their analyses of these data reveal that the following probable retorting conditions occurred in each zone of the retort:

Zone 1: Retort ignition; high temperatures, probability 1100 - 1300 C.

Zone 2: Pyrolysis; temperatures probably 500 - 700 C.

Zone 3: Oxidation at temperatures higher than Zone 2.

Zone 4: Similar to Zone 3.

Zone 5: Bottom plug of retort; low temperatures, probably less than 750 C; pyrolysis conditions.

Their preliminary analysis of distilled-water leaching data suggest that the elements studied can be conveniently organized into three major groups (Table 5-13) based on their leaching behavior in 43 core segments (Figure 5-10).

TABLE 5-13

Constituents Showing Similar Leaching Behavior from Occidental Core 3E Spent Shales (Modified from Peterson et al., 1982).

Group	Constituent
I	Conductivity Na, K, Al, Mo, Ni
II	Li, Sr, Pb, Ba, Ca, W
III	F, V, B, As, Se, Ti, Si

The occurrence of the first group of elements (conductivity and Na, Al, K, Ni, Mo) in leachates is probably controlled by the solubility of analcime, Na-feldspar, K-feldspar, and their high-temperature silicate decomposition products. The leachate concentration of these elements is inversely related to the sum of high temperature silicate products (bottom graph of Figure 5-10) for many core segments; high levels of silicates correspond to low leachate concentrations. This suggests that the solubility of these elements is controlled by the solubility of the silicate phases. This is consistent with the results of Park et al. (1980) (see Figure 5-8).

The occurrence of the second group of elements in these leachates appears to be controlled by the solubility of metal carbonates and their decomposition products (metal oxides). All of the elements in this group (for which solubility data are available) are characterized by insoluble or sparingly soluble carbonates and more soluble oxides (Dean, 1979). Although the minor mineralogy of raw and spent shales is uncertain, there is substantial evidence which suggests that Sr, Ba, Ca, and Pb occur as carbonates in raw shales (which would decompose to oxides during retorting). No data on the mineral

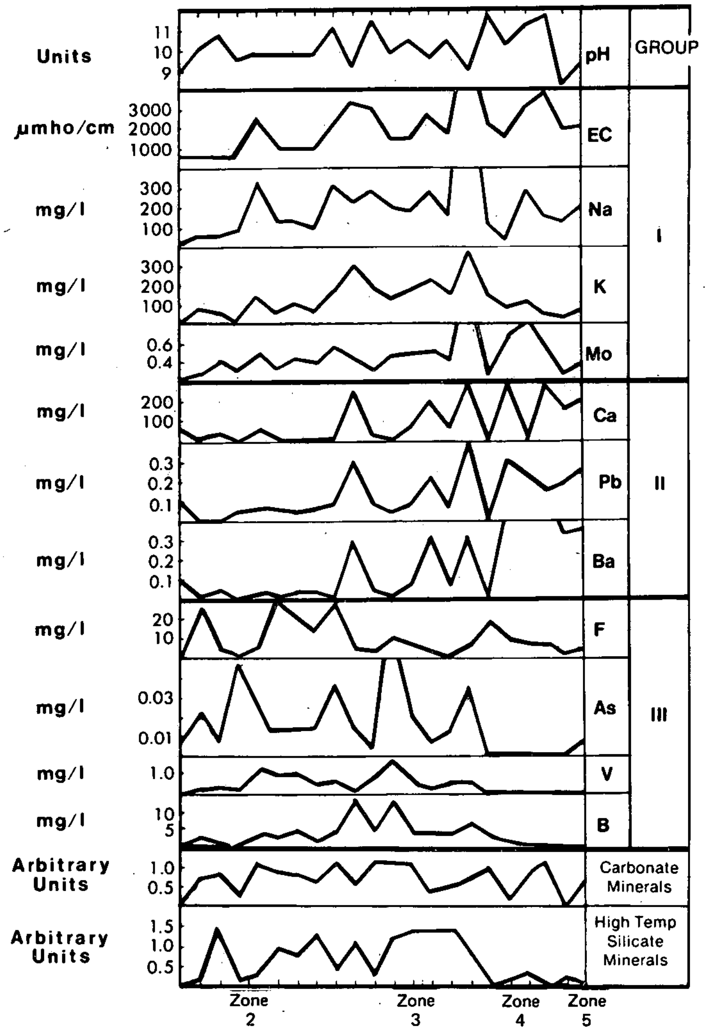

Figure 5-10. The variation in leachate composition for several sections from Occidental's Logan Wash Retort 3 corehole 3E2 (modified from Peterson et al., 1982).

residence of W or Li is known. The solid and solute chemical species for this group of elements belong to the ternary system Me^{n+}-H_2O-CO_2. [See Stumm and Morgan (1970) for a discussion of the chemistry of this system.]

The initial release of Group II elements depends on the solubility of each individual metal carbonate and oxide at alkaline pHs. A comparison of carbonate mineral levels in Peterson's spent shale cores (second graph from bottom on Figure 5-10) with leachate concentrations reveals an inverse relationship. Since the metal carbonates are sparingly soluble at alkaline pHs (Stumm and Morgan, 1970; Dean, 1979) while the oxides are more soluble, this suggests the solute concentration is controlled by carbonates and oxides.

The leaching behavior of the third group of elements (Ti, F, V, B, Si, As, Se) is more variable than that of the other two groups, suggesting several mechanisms. This group should probably be broken into several subgroups, but there is inadequate information to make the separation. The concentration of these elements in leachates is often inversely related to that of the Group II elements. Since all of these elements probably occur as anions (Fox, 1982a, Stollenwerk, 1980) (i.e., F^-, VO_4^-, AsO_4^-, $B(OH_4^-)$, their solubility is likely controlled by the alkali and alkaline earth elements in Group II, particularly Ca (due to its abundance). Studies of raw and surface spent shale leachates which have similar chemistry, have demonstrated that F is controlled by fluorite (CaF_2) (Saether, 1980; Stollenwerk, 1980). These secondary solubility controls may help to limit the concentration of these more toxic elements in field leachates. Groundwaters that will leach field in situ spent shales are alkaline and have relatively high Ca and Mg concentrations. This will promote the precipitation of the Group III elements.

Geokinetics. Krause et al. (1980) conducted experiments similar to those reported by Peterson et al. (1982) using trench samples (Figure 5-5) from Geokinetics Retort 1. They studied the mineralogy (Table 5-3) and the leaching behavior of retorted samples from five zones within Retort 1 and of a sixth sample of raw shale from below the retorted zone. They used column studies in which 200 g of -1 in. sample was packed into fiberglass-plugged 3 x 50 cm glass columns operated in a batch mode. They also used batch tests in which the samples were agitated on a ball-mill-roller drive and 50 g of -10 mesh sample was contacted with 125 mL of deionized water for 14 days. They only analyzed their leachates for pH, EC, SO_4, Mo, Se, F, As, and B, and they did not attempt to interpret their data.

We have plotted their data in the same format used by Peterson et al. (1982). An examination of the mineralogy data (Table 5-3) and the sample descriptions (Figure 5-5) reveal that the following probable retorting conditions occurred in each zone:

Zone 1:	low-temperature pyrolysis
Zone 2:	oxidation at 500-600 C
Zone 3:	oxidation at 700-800 C
Zone 4:	oxidation at 1000-1100 C
Zone 5:	oxidation at 700-800 C
Zone 6:	raw shale

An analysis of the batch leaching data presented in Figure 5-11 reveals several trends which are consistent with results reported by Peterson et al. (1982) and Park et al. (1980) (Figure 5-8). The leachate pH ranges between 10 and 11.5 for all zones except the pyrolysis zone (1) and the raw shale zone (6). This is important because it suggests that lime is present and coexists with high-temperature silicates and because the otherwise inert high-temperature silicates are soluble at these pHs. This suggests that leachate pH control could be used as a method to control in situ leachates.

The maximum leachate concentrations for most constituents (F is a notable exception) occur in Zone 3 where oxidation at temperatures of 700 to 800 C is believed to have occurred. This is consistent with leachate concentration maxima noted by Park et al. (1980) and Peterson et al. (1982) (see Figure 5-8). The behavior of F, as noted previously, is controlled by the secondary mineral phase CaF_2.

The patterns in leachate concentrations evident in Figure 5-11 are consistent with those noted by Peterson et al. (1982) and summarized in Table 5-13. The Group I constituents, EC and Mo plus SO_4 display similar leaching patterns in all zones, but do not appear to be significantly correlated with silicate minerals. There are no common patterns in the leaching behavior of the Group III elements F, As, Se, and B as also noted by Peterson et al. (1982) (Figure 5-10). All are probably anions in these leachates and may be controlled by Group II elements, which were not measured by Krause et al. (1980). It is interesting to note that the concentrations of F and As are inversely related in Geokinetics leachates (Figure 5-11) and not in the Occidental leachates, (Figure 5-10) suggesting different chemical controls.

Krause et al. (1980) also studied the effect of leaching on spent shale mineralogy (Table 5-3). He performed x-ray diffraction analyses of unleached and leached -10 mesh and -1 in spent shale from each zone. There were no significant changes in the bulk mineralogy of samples from Zones 1, 3, and 4 while changes were apparent in Zone 2 and 5 samples. In Zone 2, leaching appears to have decreased spurrite-larnite and increased the primary silicate phases quartz and plagioclase, while in Zone 5, leaching increased spurrite-larnite and decreased the primary silicates.

These investigators made several interesting observations which suggest that in situ spent shales may be more reactive chemically than others have suggested (Smith et al., 1978b) and than would be indicated by the mineral phases present. They used transmission electron microscopy to demonstrate the presence of significant quantities of glass (estimated at the percent level) in Geokinetics spent shale samples. This is important when considering leaching characteristics because glasses generally are more reactive and more soluble than their equivalent crystalline solids because of their inherently higher free energies. Thus, these spent shales are more reactive than if they had been completely crystallized. The presence of glass, rather than crystalline phases, suggests that a silicate liquid was present at some time during retorting and that the retort cooled fast enough so that crystallization could not proceed to completion. This observation suggests that retort cooling procedures can be used to affect the leachability of the resulting spent shale. Krause et al. (1980) also noted that the high-temperature silicate minerals were extremely fine grained (about 1000 Å)

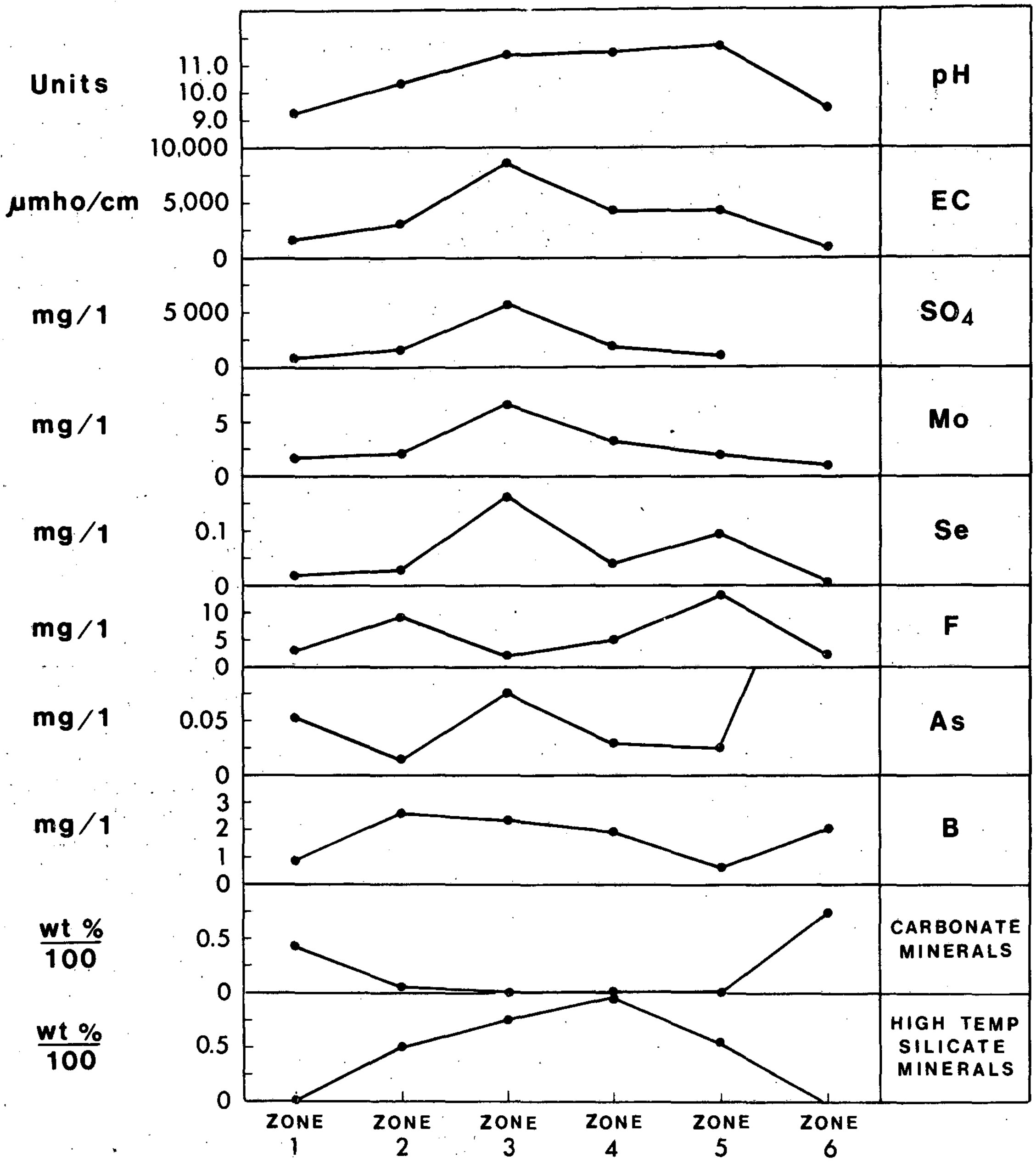

Figure 5-11. Variation in leachate concentration (batch leaching of -10 mesh material, 0.40 g/mL for 14 days) in Geokinetics Retort 1 (modified from Krause et al., 1980). The detailed mineralogy for these samples is presented in Table 5-3.

and that defect structures and grain-boundary dislocations were common. Both of these factors increase the normal solubility and reactivity of these so-called inert silicate phases.

Leach Water Quality and Temperature. Most laboratory leaching studies have been conducted with distilled water under ambient conditions. In the field setting, alkaline groundwaters with high concentrations of Ca, Mg, Na, or SO_4 may contact hot to warm spent shales. The influence of leaching atmosphere (U.S. DOE, 1980), of water temperature (Amy, 1978; Bethea et al., 1981), and of water quality (Peterson et al., 1982; Bethea et al., 1981; Amy, 1978) on leachate composition have been studied. These investigations reveal that the temperature and quality of leach water exert a significant control over the inorganic quality of leachates. Leaching atmosphere does not appear to be as important.

Peterson et al. (1982) and Amy (1978) compared leachates developed using distilled water and groundwaters. Peterson et al. (1982) used their standard leaching test (0.2 g/mL for 48 hrs) to investigate the effect of groundwaters from the upper and lower aquifers at Tract C-a on the composition of leachates derived from several samples of Logan Wash spent shale. Some of Peterson's results for upper aquifer leach water are displayed in Figure 5-12. Peterson noted a significant difference in the chemical composition of leachates generated with distilled water and groundwater. These studies revealed that, for most samples, the concentrations of inorganic carbon, Ca, Ti, Fe, Pb, Co, Al, Ba, and Ni were significantly lower in groundwater leachates than in distilled water leachates; and that organic and inorganic carbon were removed from native groundwaters. These effects were hypothesized to be due to precipitation with ligands such as CO_3, OH, or SO_4. The concentrations of other elements--B, Mo, V, K, and Li--were about the same in groundwater and distilled water leachates while the concentration of Na was approximately equal to the sum of the concentrations of Na in the groundwater and in the distilled water leachate suggesting that Na is nonreactive. Equilibrium models are presently being used to interpret these results (Peterson, 1981).

Amy (1978) studied the effect of a synthetic groundwater and two water temperatures (20 C and 80 C) on the leachability of total organic carbon from four samples of simulated in situ spent shale (Table 5-7). Amy's synthetic groundwater, prepared from 6 g $NaHCO_3$, 2 g NaCl, 1 g Na_2CO_3, and 1 g Na_2SO_4, had a conductivity of 12,000 μmhos/cm and a pH of 9. Some of his results for two spent shales are shown in Figure 5-13. The synthetic groundwater did not effect the leachability of TOC at a water temperature of 20 C. However, at 80 C, the synthetic groundwater enhanced the leachability of TOC from inert-gas-run spent shales (Types 2 and 4) and inhibited the leachability of TOC from combustion-run spent shales (Type 1 and 3). Since the nature of the organics in these leachates is poorly understood, it is not possible to formulate mechanisms for this behavior. Amy's studies also revealed that elevated leaching temperatures increase the amount of TOC that is solubilized for all of the spent shales except that from a gas recycle run (see Table 5-7).

Bethea et al. (1981) also investigated the solubility of several major and minor ions for two leach water temperatures (35 and 90 C) using two different Utah groundwaters (Table 5-12). Their results are consistent with known relationships between solubility product and temperature.

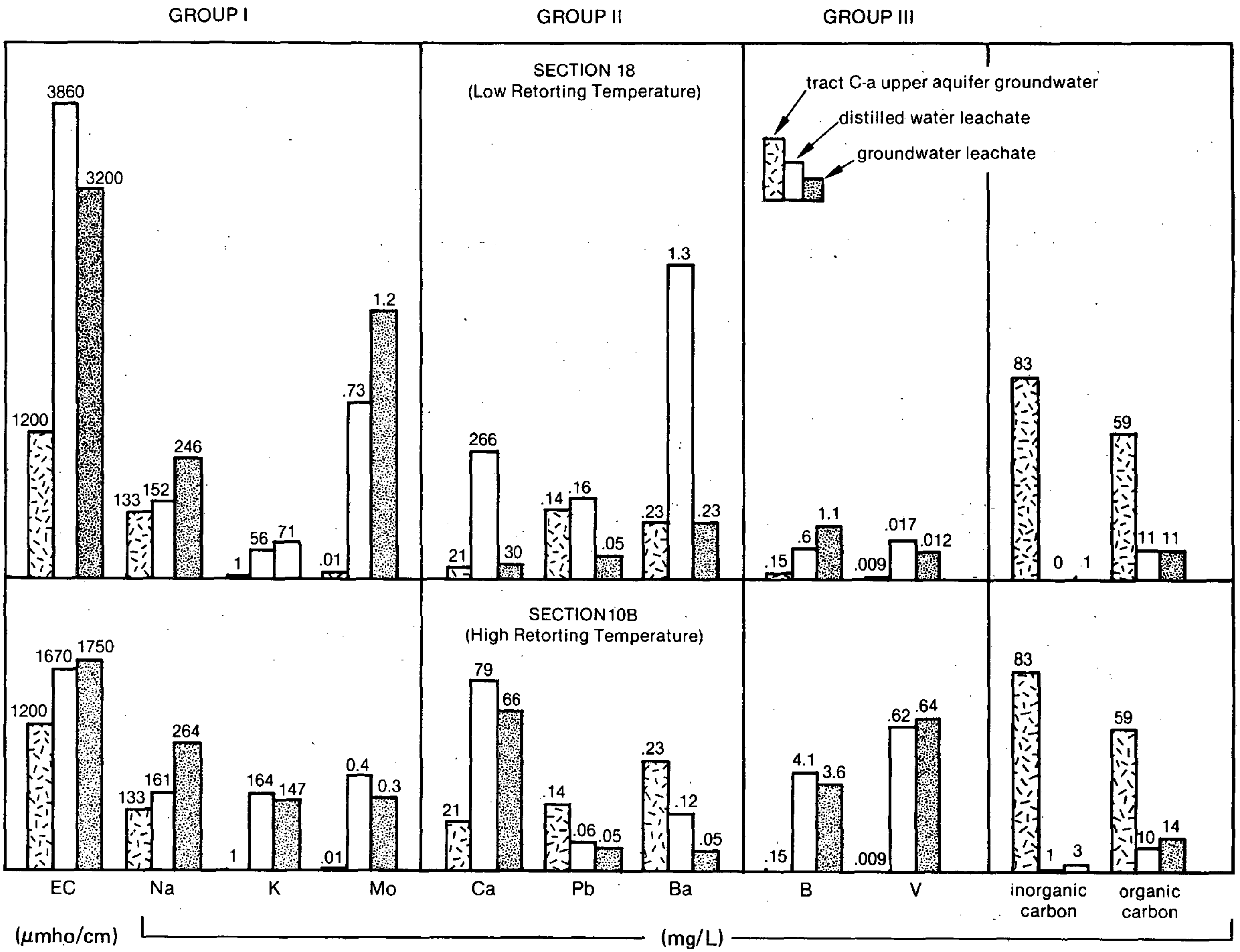

Figure 5-12. The effect of groundwater from the upper aquifer at Tract C-a on the quality of leachate derived from Occidental Logan Wash spent shales (modified from Peterson et al., 1982).

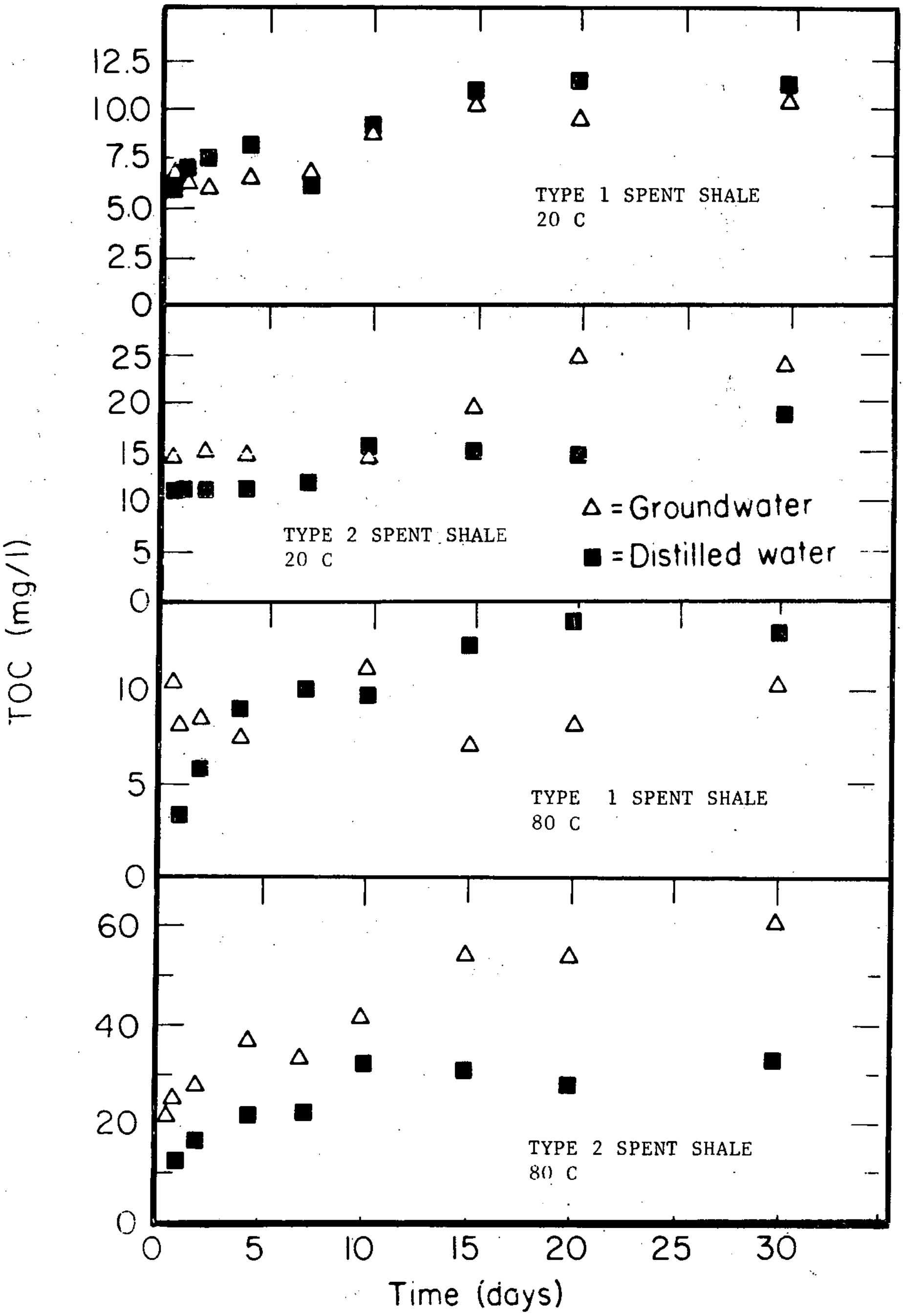

Figure 5-13. The effect of synthetic groundwater and leach water temperature on the solubility of total organic carbon (TOC) from two different types of simulated in situ spent shales (see Table 5-7 for spent shale information). Modified from Amy, 1978.

Their studies show that leach water temperature had no effect on pH or F. The elevated temperature increased the solubility of Na and K and decreased the solubility of Ca and Mg in the Douglas Creek groundwater leachates. Other results were variable. Bethea et al. (1981) proposed that these effects were due to increases in the diffusion coefficient with temperature and to changes in solubilities of primary and secondary mineral phases with temperature. In particular, they noted that the solubility of KOH increases and that of $Ca(OH)_2$ and $CaSO_4$ decrease with temperature.

The effect of atmosphere on the leachability of various ions was studied by PNL using spent shales from Occidental corehole 3E1 (U.S. DOE, 1980). The samples were packed in small columns and equilibrated under water-saturated nitrogen and ambient atmospheres. The investigators concluded that atmospheric conditions under which the leaching occurred did not significantly affect the composition of leachates. Reduction in pH and a significant elevation in carbonate alkalinity of the ambient leachates were attributed to increased partial pressure of carbon dioxide. This is consistent with results reported by other investigators (i.e., Taylor et al., 1982) for surface spent shale and previously discussed on page 4-31. The presence of oxygen had little effect on the magnitude of soluble carbon and on the behavior of other components (U.S. DOE, 1980).

Surface Properties. The surface area, electrical charge, and texture of spent shale will affect leaching rate and leaching mechanisms. Desorption/sorption and ion exchange reactions depend on the number of surface sites exposed to the liquid. Surface texture affects surface area, and a surface which is highly textured, such as in situ spent shales (Krause et al., 1980), may be expected to be more soluble and reactive than their smooth equivalents. And surface charge will influence subsequent ion exchange reactions between spent shale and dissolved constituents.

Some of these properties have been investigated as they relate to the leaching of in situ spent shales (Jackson et al., 1975; Amy, 1978; U.S. DOE, 1980). Jackson et al. (1975) studied the effect of three spent shale particle size ranges (1-3 in., 3-6 in., 6-12 in.) on the concentration of 16 constituents. He used batch leaching tests in which 1 g of spent shale (from LETC 10-ton retort) was contacted with 10 g water at 25 C and stirred for 5 minutes. There was no relationship between particle size and leachate concentration for any of the parameters that he studied (Ca, Mg, Na, K, B, CO_3, HCO_3, SO_4, Cl, NO_3, F, TDS, DOC, pH). Potassium and Cl concentrations were the same for all three particle sizes while for most other constituents, the intermediate size fraction (3 - 6 in.) displayed either the highest or lowest concentration among the three reported. This suggests that his samples may not have been uniform among the three size fractions.

In other work, Amy (1978) studied the effect of particle size on pH, EC, and TOC. He studied two particle size ranges, 0.14 to 0.28 cm and 0.28 to 0.64 cm, in quiescent batch tests in which 50 g each of four spent shale (see Table 5-7) were contacted with 50 mL distilled water for time periods ranging from 0.5 to 30 days. He found that the concentration of TOC and EC and the pH were consistently higher for the smaller particle size, suggesting that a surface interaction was important in establishing the concentration of these constituents.

In other work (U.S. DOE, 1980) the electrophoretic mobility and zero point of charge was determined for 11 samples from Occidental core 3E1. These measurements demonstrated that Occidental spent shale has a net negative charge above a pH of approximately 2.7. Similar results have been obtained for many surface spent shales. This indicates that dissolved cations (Ca, Mg, Na) may be sorbed to spent shale following their initial release from the solid.

Experimental Variables. Others have studied the effect of equilibration time and solid-to-liquid ratio on leachate composition and leaching rate. This approach has been used with surface spent shales to help identify the mechanism(s) that control leachate concentration (Saether, 1980; Glaze, 1981) and was discussed on page 4-79. A similar approach has not been employed for in situ spent shale although several investigators have used these experimental variables in preliminary screening studies (Peterson et al. 1982; Amy, 1978). This work will be briefly overviewed here.

Peterson et al. (1982) studied three samples of Occidental core material. Each was leached for 2, 7, and 28 days in batch tests using a solid-to-liquid ratio of 0.4 g/mL. The behavior of ions as a function of leaching time can be summarized as follows: (1) concentrations of B, Co, and Ni increase with time; (2) concentrations of Mo and K are constant with time; (3) concentrations of Al, Ca, Li, Si, Sr, Na, and V decrease but level out after 7 days; (4) concentrations of Ba, Fe, Pb, Mg, Sn, Ti, W, and Zn show no discernible trends; (5) concentrations of Be, Cd, Cu, Mn, and Hg were below detection limits; (6) no data were available for As, F, and Se.

In other work, Amy (1978) studied the effect of contact time and solid-to-liquid ratio on the concentration of TOC. His data is too voluminous to go into in detail, and the reader is referred to his thesis. In general, his studies demonstrated that sorption/desorption mechanisms control the concentration of TOC in his simulated in situ spent shale leachates. However, there was evidence that secondary solubility was the controlling mechanism for some samples under certain conditions.

ENVIRONMENTAL TRANSPORT AND EFFECTS

Previous sections have considered the formation and transport of leachates within an in situ retort. This section reviews laboratory, field, and modeling studies that have considered extra-retort transport and environmental effects of in situ spent shale leaching. Groundwaters that reinvade an in situ retort and solubilize materials from the spent shale, may migrate through the retort and into adjacent aquifers. These leachates eventually may discharge into streams and springs or be withdrawn in wells where they may come into contact with water users.

The potential for this occurrence and its importance are controversial issues which cannot be solved readily with existing analytical techniques and data. The principal problems are related to: (1) inadequate field data to describe the hydrogeologic system, (2) absence of adequate analytical techniques and field data to predict water and solute transport in fractured media; (3) inadequate field data to determine if surface streams and springs are hydraulically connected to the upper aquifer, and (4) absence of data on leachate transport properties.

Environmental Transport

In situ leachates will migrate through fractured oil shale aquifers, eventually discharging through wells, springs, and streams. A variety of chemical, physical, and biological transformations will modify the composition of these leachates during transport. These interactions may include ion exchange, precipitation, sorption, dispersion, and others.

Field and modeling studies have been conducted to explore these types of interactions. However, no laboratory studies have been conducted on the transport of in situ leachates, and work is required in this area. The information previously reported on surface spent shale leachate transport is broadly applicable to the analogous in situ leachate transport problem. However, differences in the geologic material through which the leachates move limit extrapolation of distribution coefficients (Table 4-26) developed by these investigators (Glaze, 1981; Runnells and Esmaili 1981, 1982) to in situ leachates.

Field Studies

Field monitoring studies are being conducted at several experimental in situ sites. Studies are in progress at the LETC Rock Springs site, at Occidental's Logan Wash site, and at the Rio Blanco Oil Shale Co.'s Tract C-a site. The results of these studies are difficult to interpret due to chemical analysis problems, the large quantity of data generated which requires sophisticated statistical treatment, and the absence of adequate site geohydrologic data and a suitable conceptual framework for data analysis. Many of the studies are also new, and there are not enough data to assess long-term trends. However, the available literature does indicate that in situ retorting will modify local groundwater quality. Studies at each experimental site are reviewed briefly here.

Rock Springs. The Laramie Energy Technology Center (LETC) has been conducting pre-, operational and post-burn monitoring at their true in situ experimental site near Rock Springs, Wyoming. This site has been used since 1966 to evaluate various fracturing techniques associated with a true in situ process. These experiments were based on the concept of igniting the shale in an injection well and then forcing combustion products to recovery wells located in a ring around the injection well. Nine individual experiments were conducted at different sites. Oil yields were low due to failure of the fracturing techniques to produce adequate porosity in the formation, and the program has been abandoned. Pertinent geological and hydrological data for this site have been reviewed by Glover et al. (1982).

Extensive environmental monitoring has been conducted at four of these sites (4, 6, 6A, and 9) by LETC (Jackson et al., 1975; Virgona et al., 1979) and the U.S. Geological Survey is presently conducting a field and modeling study at sites 4 and 9 to evaluate water and solute transport (Glover et al., 1982).

The monitoring programs at these sites have consisted of a series of pattern wells in the retorted region surrounded by distant observation wells. Standard water quality parameters and major, minor and trace elments have been measured prior to, during, and proceeding the burns. Much of this work is inconclusive due to analytical problems, inadequate information on local geohydrology, and the absence of a conceptual framework within which to evaluate the data. However, the data do show changes in groundwater quality attributed to the retorting experiments. In particular, local groundwaters initially were sodium carbonate-bicarbonate. During and subsequent to retorting, there was a clear increase in carbonate and bicarbonate ions. Boron and TOC levels also increased with time. The TOC returned to background levels but the B concentrations remained high. There was no other consistent changes in quality, and sulfate, COD and other parameters increased in some wells and decreased in others (Virgona et al., 1979). The evaluation and analysis of the large amounts of data collected at these sites will require more sophisticated techniques than those employed to date.

Occidental. The Occidental Oil Shale Company has conducted pre-, operational, and post-burn monitoring around Retort 6 at their Logan Wash experimental site. This program, initiated in mid-1975, has included measurements for up to 77 parameters from 31 different wells and surface water sites.

The data resulting from that program have been analyzed by Meglen and Erickson (1981) using pattern recognition techniques to identify water quality changes associated with retorting. These investigators found very few water quality changes that could be attributed to the transport of leachates and other fluids from the retort. The only significant changes that they reported were increased Li concentrations at one stream site; increased B, K, and alkalinity at two satellite wells close to the retort site; and increased Mg, SO_4, and K at a satellite well located at distance from the retort. They also provided evidence for a subtle regional change in water quality.

Geokinetics. Geokinetics has conducted field studies at their Seep Ridge site similar to others described above. Preliminary results from one such study (Hutchinson, 1979) demonstrated that retorting does result in changes in groundwater quality. However, the large volume of data, analytical problems, and lack of information on geohydrology limited the utility of this study. They have planned other studies for this site to resolve some of these problems (Law, 1982).

Modeling Studies

The transport of leachates away from in situ retorts has been investigated using solute transport modeling techniques (Fox, 1980b; Robson and Saulnier, 1981). The modeling techniques are far more sophisticated than input data warrant, and both of these studies were hampered by the absence of transport data such as distribution and dispersion coefficients and adsorption and ion exchange isotherms. However, it is noteworthy that the conclusions from these two studies, which used very different techniques, are consistent. Fox (1980b) concluded that it could take centuries before significant groundwater degradation would occur due to the low flow velocities in many areas of the Basin. However, the report pointed out that the potential long-term effects could be serious due to the critical issue of salinity in the Colorado River system and the slow self-purification properties of groundwater aquifers. Leachates could result in salinity increases in the Colorado River at Lees Ferry of from 2 mg/L to 56 mg/L and in the Piceance Creek at White River of from 1740 mg/L to 46,100 mg/L. These estimates recently have been revised by Persoff and Fox (1982) to conform with more recent laboratory studies of in situ leachate composition. Their revised estimates predict an increase in TDS in the Piceance Creek at White River of 5200 mg/L and in the Colorado River near Lees Ferry, of 6 mg/L. Robson and Sauliner (1981) similarly concluded that several centuries after site abandonment the discharge of leachate from in situ retorts would adversely affect the quality of local surface waters and groundwaters. For Tract C-b, they predicted a 750 mg/L to 1750 mg/L increase in TDS of Piceance Creek after 60 years of leaching and a 20,000 mg/L increase near the mine. Similarly, for Tract C-a, they predicted minimal changes in water quality in Yellow Creek following 60 years of leaching due to low flow velocities and long transit distances, and an increase in excess of 40,000 mg/L near the mine.

Other similar modeling studies should not be conducted until input data are better defined. In particular, geohydrologic parameters, including porosity, permeability, and information on fractures and transport parameters, particularly distribution and dispersion coefficients, are required.

Environmental Effects

The importance of in situ leachate transport ultimately depends on the effect the leachates will have on local water users. Such effects are usually evaluated by biological testing and by comparing leachate composition with water quality criteria and standards.

Peterson et al. (1982) compared the quality of their Occidental leachates with predevelopment groundwater quality and with various water quality standards and criteria. [The only constituents among those studied (see Table 5-5) that were elevated in leachates and not in groundwater and which therefore, may alter the beneficial use of the water, were Se, Pb, and V.] They noted that concentrations of Pb and Se in groundwaters contaminated with leachates may exceed federal drinking water standards and that Pb and V may exceed livestock watering criteria while V may exceed recommended irrigation criteria.

The authors are not aware of any relevant biological testing data for in situ leachates. The U.S. Department of Energy (1980) presented some Ames mutagenicity data for column leachates from Occidental Core 3E1 materials. Five out of 24 samples tested showed Ames activity. However, the significance of this data is uncertain because the core was contaminated by polymers used during drilling.

Chapter 6

LEACHING PLAN

This review reveals that, while a great deal of work has been conducted on oil shale leachates, a theoretical framework is still missing and many important areas have been overlooked or inadequately studied. This chapter advances some general and specific recommendations for future leaching research. Research needs that are common to all types of leachates (surface, in situ, and raw) are presented in the section on "General Recommendations" while recommendations that are specific to each leachate type are discussed in separate sections on "Raw Shale Leachates", "Surface Spent Shale Leachates", and "In Situ Spent Shale Leachates".

GENERAL RECOMMENDATIONS

These recommendations apply to all types of leachates discussed in this report, and they address the approach to and management of such research. Most past and present work is characterized by an emphasis on detailed elemental analysis of leachates under specific and narrowly defined conditions without consideration of mineral solubilities, of inter- and intra-particle mass transport, or of other fundamental phenomena. Results of these studies are little more than tabulations of concentration data valid only for a given material and a specific set of conditions. Such data are not useful for predictions of environmental transport and effects, and they do not significantly advance our understanding of mechanisms and kinetics of leaching. This existing program also has been replete with duplication and analysis of nonrepresentative or poorly documented samples.

Future research should emphasize basic research directed at understanding physical, chemical and biological mechanisms and kinetics of leaching. Six modifications in and additions to the existing program are specifically recommended. The first two of these have been recently initiated at the institutions indicated in parentheses following the recommendation. These programs should be encouraged. The six general recommendations are:

- Geochemical and mass transfer models should be developed for raw, surface, and in situ leachates and used to integrate existing information into a coherent theoretical framework and to help identify additional information requirements (PNL, LANL, University of Colorado).

- A systems approach, which elucidates the interrelationship among raw shale, processing parameters, spent shale, and leachates, should be adopted (LANL).

- Future leaching studies should utilize samples from small laboratory reactors which are generated under carefully controlled and well-defined conditions, and research should be decoupled from industry plans.

- The available data should be analyzed to determine the environmental risks of leachates to help focus the program on key issues.

- A standard leaching protocol and standard samples should be developed and used to calibrate and validate leachate results.

- Better coordination among agencies which fund oil shale research is required, and funding officers should encourage investigators to publish results in refereed and archival journals, rather than in obscure research and progress reports.

Each of these recommendations is discussed here.

Modeling Framework

Geochemical and mass transfer models describe the physical and chemical relationships among leaching variables. They are indispensible in designing meaningful leaching experiments and in interpreting the results of such experiments. They also facilitate the integration of existing information into a coherent theoretical framework, and they help to identify information needs.

Part of the present disarray of the leaching field is due to the absence of a theoretical framework of the leaching process. Many past leaching studies have been little more than detailed characterization studies of shales and leachates without consideration of fundamental variables. Extrapolation of this type of data to other materials or conditions is impossible.

It is strongly recommended that geochemical and mass-transfer models be developed before any new laboratory research is initiated. Separate models should be constructed for raw shale, surface spent shale, and in situ spent shale. These separate efforts should be closely coordinated due to many similarities among the three media. Results from model construction should be used to guide future laboratory and field leaching research.

Systems Approach

Most leaching research has been very narrow in focus, emphasizing one aspect of leachate production in the absence of other important variables. A broader, systems approach that recognizes the interrelationships of raw shale, processing conditions, and spent shale mineralogy needs to be adopted.

In order to understand, model, and predict leachate composition in a meaningful way, one must elucidate the interplay of raw shale and process parameters in forming the spent shale and the subsequent interaction of the spent shale with the water. This approach, shown schematically in Figure 6-1, requires the careful characterization of solids and liquids for a range of conditions. Such an approach has not been used in most leaching studies conducted to date.

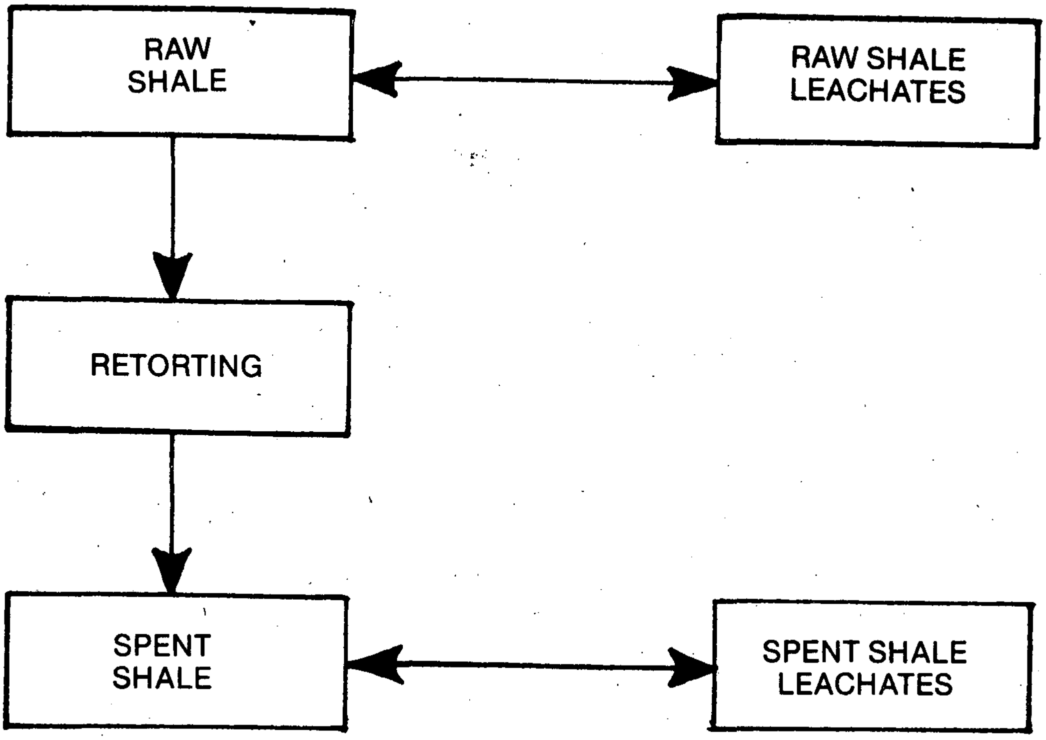

Figure 6-1. Schematic representation of the interrelationship between mineralogy, retorting conditions, and leachate composition.

Most leaching studies have attempted to identify the mechanisms that control leachate chemistry by studying the aqueous phase rather than the solid phase. Release mechanisms from the solid phase to the liquid phase have been probed by studying the effect of liquid-to-solid ratio, particle size, contact time, and other hydraulic variables rather than by studying the chemistry of the solids that supply the ions of interest. There is a strong need to couple studies of aqueous chemistry with studies of solid-phase chemistry. In particular, solids should be characterized using x-ray diffraction and microprobe techniques, and pure compound studies of mixtures of various mineral phases should be used to develop relevant solubility data. Existing analytical techniques to characterize solids need to be improved, especially x-ray diffraction.

A related problem is the investigation of a single spent shale independent of raw shale or spent shale mineralogy. Most contemporary leaching studies have extensively characterized leachates from a single sample for a limited range of a few variables. The samples studied are often not representative of commercial materials and thus, the data may not be useful or mineralogy of raw shale feeds may differ, producing wide concentration ranges in leachates of spent shales from the same process. Relating leaching characteristics to raw shale composition and retorting conditions can provide valuable information needed to sort out these and other differences among leachates. This approach is also a valuable method of overcoming data obselence due to changes in industrial plans.

Samples

Most leaching studies have used samples from near-commercial processes. This would be desirable if an oil shale industry existed and fixed commercial processes were available for study. However, no such industry exists today, and the proposed technology is in transition. Spent shale mineralogy may vary from sample to sample due to changes in feedstock or in processing conditions. In other cases, representative samples of spent shale from near-commercial processes may not be available due to sampling problems (in situ technologies), to the lack of adequate quantities of material for research purposes, or to proprietary nature of the process. Analogously, the near-commercial samples are generated for process research and proper care is not taken to prevent sample alteration or to document sample history.

We recommend that future laboratory leaching studies emphasize spent shales produced in small, laboratory reactors operated under carefully controlled and well-defined conditions. (Limited studies should be conducted on near-commercial processes to obtain characterization data or leachates for environmental assessments.) Well-instrumented retorts, such as LLNL's simulated in situ reactors and its fluidized-bed reactor, should be run for a range of conditions, selected by "technology" experts to span the range expected in commercial plants. Special sampling procedures should be developed to minimize contamination and to guarantee sample integrity (i.e., to prevent breakage, air oxidation, etc.).

The resulting samples should be used to conduct fundamental research on the effect of processing conditions (temperature, gaseous atmosphere, heating rate, etc.) on spent shale mineralogy and leaching behavior. The resulting conceptual framework should be used to help evaluate the results of other studies using near-commercial materials.

Assessment

The environmental significance of the rapidly accumulating leachate data base needs to be put into perspective to help establish future research priorities. The potential importance of leaching depends on the risks that leachates may pose to ecosystems, human populations, agriculture, and other potential users of local water supplies. The magnitude of any risks depends on the composition and volume of leachates that migrate beyond the pile or in situ retort and on subsequent chemical and physical transformations.

Although considerable additional research is needed on transformation, transport, and effects before precise predictions are possible, there is adequate information to make order of magnitude estimates of effects and to evaluate differences among process and disposal options. Existing computer models of spent shale systems (i.e., Hall, 1982; Margheim, 1975; Fransway, 1980) and leachate data can be supplemented with calculation procedures and analytical data developed for related systems (i.e., Southworth et al., 1982; Mackay and Peterson, 1981; Mackay and Shiu, 1981; Schwarzenback and Westall, 1981; Mackay, 1982) to estimate environmental risks.

Standard Leaching Test and Samples

It is recommended that a standard leaching protocol and raw and spent shale samples be developed and used to calibrate and validate leachate results. Such a test would not replace the usual experimental methods, but rather, complement them. Different experimental techniques and variables are necessary to study different phenomena or to generate leachates for various purposes, and thus, uniform procedures are not appropriate. However, this study clearly demonstrates that there is a need to calibrate and compare results obtained in different laboratories and with different samples. A standard test and standard samples would achieve this.

Available leaching data have been generated over more than a decade by many separate research groups using different analytical techniques (of unknown accuracy), samples, and leaching procedures. Samples of widely varying histories (ages, exposure to weathering, and so on) have been studied. And during this period, the samples themselves have changed due to evolutions in retorting technology. Thus, it is difficult to interpret the data and separate out differences due to experimental techniques from those due to sample history or the variables under study.

The use of a standard leaching test (which would have to gain acceptance by "consensus" rather than enforcement, if it is to be effective) and a standard raw and spent shale could alleviate these problems. These standards, much like NBS reference materials, would be used in conjunction with other techniques and materials, not in place of them. Such samples would be analyzed prior to initiating a series of experiments or intermittently throughout them, to validate analytical techniques and to provide consistent and comparative information on a set of samples.

Coordination

It is recommended that additional management steps be taken to better coordinate future leaching research and facilitate information transfer. Considerable duplication is evident in the leaching studies that have been conducted over the past decade. This is due, in part, to the large number of organizations that have both funded and conducted the work and to the difficulty of identifying and acquiring others' research reports. This could be alleviated by further improving communication channels among the various sponsoring and performing organizations, and by encouraging publication in refereed and archival journals and by sponsoring a symposium on leaching which would include all research participants and their sponsors. In the long-term, it may be useful to establish an official, interagency task force and computerized library system to help coordinate research efforts and to facilitate identification and acquisition of research reports.

SPECIFIC RECOMMENDATIONS

Raw Shale Leachates

Very little research has been conducted on the leaching of raw shales, compared to spent shales. Studies completed to data demonstrate that raw shale leachates may be toxic to aquatic organisms and that several trace elements are sufficiently elevated to be of environmental concern, notably, B, F, Li, and Mo. Our evaluation and assessment of the research summarized in Chapter 3 indicate that additional or new research is required to better define the potential environmental importance of raw shale leachates. This research should emphasize laboratory studies designed to develop a mechanistic understanding of the leaching process. The following specific studies are recommended:

Samples

- subore, overburden, and fines from proposed developments
- feedstocks for Superior, Union, Chevron
- feedstocks for proposed development sites in Utah

Characterization

- chemical speciation of inorganics, organics, and organometallics

Field Conditions

- Leach water quality

Mechanisms

- Release and transport of pH, TOC, TDS, SO_4, NO_3, B, Mo, Li, Zn, As, Mn, Eh
- thermodynamic, kinetic, and hydrologic data for important physical, chemical, and biological processes
- mineralogy/solubility

Simulations

- coarse-ore stockpile
- fines reject pile
- subore and overburden storage

Most experimental studies on the leaching of raw shales has focused on samples from the Colony Mine, the Anvil Points Mine, and Tract C-a. Additional work is in progress to evaluate leaching characteristics of Logan Wash and Tract C-b samples. Samples from additional geographic areas and stratigraphic zones should be investigated. In particular, there is presently limited information on the leaching behavior of raw shales that will be used in proposed Superior, Union, and Chevron developments in Colorado, and only a single sample of Utah shale has been leached. The present intensification of development in Utah suggests that Utah raw shales should receive priority in the near term.

Characterization studies have focused on total elemental concentrations and major ions. Although the concentration of organic carbon in raw shale leachates is quite high, no work has been published on the compounds present. Chemical speciation studies are needed to determine the fate and effects of metals and organics in the environment.

Mechanistic studies have focused on F, B, and Mo, and they have attempted to qualitatively explain observed leaching characteristics. Additional work is needed to improve our understanding of these and other elements (B, Li, Zn, As, Mn). Quantitative mechanistic models should be developed for environmentally important elements for use in predictive solute transport models. The stoichiometry and kinetic and equilibrium constants for rock-water interactions and aqueous reactions should be determined. These studies should consider the effects of particle size, solid-to-liquid ratio, contact time, and mineralogy. Experimental techniques and standards should be developed that simulate field conditions.

Very little work has been initiated in the area of water and solute transport. It was previously believed that raw shale piles did not pose an important environmental threat because soils and natural geologic material consist of weathered oil shale. However, work completed to date demonstrates that leachates from freshly mined oil shales contain elevated (compared to background) and environmentally significant concentrations of a number of elements including F, B, Mo, As, Li, and Zn and aquatic toxicity tests reveal that some raw shale leachates are toxic to Daphnia and fathead minnows. Thus, work is needed to evaluate the potential for water and solute movement in various types of raw shale piles. This was previously discussed under "General Recommendations". These simulations should consider fines reject, coarse ore, subore, and overburden storage piles, and they should include regions proximate to the piles, viz. overland flow downslope from the pile and percolation through underlying strata. These studies should be coordinated with laboratory and field work to determine key input variables including porosity, saturated and unsaturated properties, media characteristics, boundary conditions, dispersion and diffusion coefficients, etc.

Surface Spent Shale Leachates

A considerable amount of research has been conducted in the past decade on the leaching of spent shales from surface processes. This work has revealed, not unexpectedly, that the leaching process is highly complex, depending on a myriad of physical, chemical, and biological processes. However, this work has been constrained by the absence of a consistent theoretical/conceptual framework, and studies have tended to emphasize disparate aspects of the leaching process in isolation from other important variables. In other instances, leaching data have been generated in conjunction with other types of studies, such as revegetation or cementation, and the resulting data, an adjunct to the original study, has not been reduced or analyzed. And the spent shales under study have undergone a gradual transition as industry has modified its retorting technology.

Thus, there is considerable variability and disparity among published leaching studies and for leachate compositions. We still do not have accurate and representative characterizations of leachates from near-commercial processes, and we know very little about the environmental significance of these leachates. There is an urgent need to develop a consistent theoretical framework to guide and organize future research and to develop standard test methods and samples to provide a common reference point among future studies, as discussed previously.

Evaluation and assessment of the research summarized here indicates that additional or new research is required in the following areas:

Samples

- Lurgi, Chevron, Union, Superior
- improved sample history documentation
- consistent comparison of different processes
- codisposed solids (e.g. catalysts)

Characterization

- chemical speciation of inorganics, organics, and organometallics

Field Conditions

- codisposal/volatilization
- revegetation
- catchment dam
- post-abandonment
- field validation of laboratory procedures
- leach water quality

Mechanisms

- release and transport of F, B, Mo, Li, pH, S, TDS, Eh
- thermodynamic, kinetic, and hydrologic data for important physical, chemical, and biological processes
- stoichiometry and kinetics of rock-water and aqueous-phase reactions
- microbial interactions

Simulations

- cross-valley fill
- side-hill fill
- surface pile
- backfilled mine
- pile construction
- effect of pile on natural recharge
- water movement, particularly infiltration of snowmelt

Although future research should emphasize samples from laboratory reactors, limited characterization data on leachates also should be obtained for use in environmental assessments and biological testing programs. The suite of near-commercial process samples that has been studied should be expanded. The majority of leaching studies has used TOSCO II or Paraho spent shales. No data have been published on Lurgi and Chevron STB spent shales, a single study has reported leachate data for a Superior sample, and three studies of limited scope have addressed Union spent shales. Work similar to that reviewed or recommended here should be undertaken for these and other samples. The results from these studies should be coordinated with leaching studies using spent shales from laboratory reactors to help interpret the data.

The variability of available leachate data could be reduced if better documentation of sample origin and history were provided. Research reports should include information on process of origin (Union A, B, or SGR); stratigraphic origin of feedstock (Mahogany Zone, Mahogany Ledge); date of run; run conditions (when available); and history of the sample prior to receipt (disposal pile, sealed drum, age, etc.). Any anomolous conditions, such as postcombustion or moisturization, also should be noted. This type of documentation is particularly crtical for work involving organics because they are readily oxidized and biodegrated.

Very little realistic characterization data have been generated for surface spent shales. Although there are many measurements of leachate composition, experimental conditions often do not simulate those expected in the natural environment. Long-term field studies should be conducted in conjunction with realistic laboratory tests to determine the composition of percolates and runoff.

There is a need to develop and validate methods and ranges of variables that simulate long- and short-term field leaching in the laboratory. Important field variables, such as solid-to-liquid ratio, porosity, particle size, and leach water composition, need to be specified to simulate field conditions. Leaching methods that yield realistic characterization data need to be developed and used in a consistent manner on a wide range of spent shale samples.

Additionally, available characterization studies have focused on total elemental concentrations and major ions. Although organic carbon concentrations of these leachates are high, only a few compounds at the ppb level have been identified and quantified. Assessment of environmental impacts and chemical modeling of the leachate system will require detailed chemical speciation data. Methods should be developed to speciate inorganics, organics, and organometallic in surface spent shale leachates.

Several process-specific or disposal-related variables will affect the quantity and quality of leachate. The effect of some of these on short- and long-term leachate quality have not been adequately studied. Additional study of codisposal of liquids and solids, and the related issue of volatilization, is required. The effect of codisposed solids, such as catalysts, on leachate quality should be assessed. Organic and inorganic compounds in moisturization waters have been observed to sorb onto spent shale. Future mobilization of these materials under natural conditions should be explored. The potential volatilization of codisposed substances through photodecomposition or biological alkylation and degradation pathways should be investigated.

Catchment dams, constructed out of highly compacted spent shale, will be constructed downstream of the piles to collect and store runoff from the pile surface. The water stored behind these dams will be used for in-plant purposes during the life of the project. Sediment, composed of spent shale fines, will settle out and collect at the bottom of the reservoir. This sediment, and the spent shale containment, release soluble materials and degrade the stored water. This may be particularly significant if waterfowl and wildlife use the catchment or if seepage from the dam reaches the water table. The significance of this occurrence has not been addressed.

The environmental integrity of the surface drainage systems on site abandonment should be assessed. Pile runoff is controlled by routing upstream runoff around the pile and by collecting water from the pile surface in a series of diversion ditches and storing it behind the catchment dam. The high sediment content of these runoff waters may silt out the diversion structures and dams if they are not maintained on abandonment. This could lead to overflows and impact water quality. This issue needs to be studied using computer modeling techniques.

Finally, the surface of the disposal pile will be reclaimed. Procedures will vary depending on the specific spent shale. These reclamation procedures will dramatically affect water movement and leachate composition. Although work has addressed pH, salinity, and sediment, a wider range of variables and chemical constituents needs to be studied. And the existing data needs to be reduced, analyzed, and used to develop or validate computer models. Completed work suggests that the surface of the pile (soil layer plus vegetation) can be designed to retard moisture movement. This concept should be pursued in field work.

Perhaps the single most important research need is for the development of a mechanistic water-solute transport model of the pile and extra-pile environment, as discussed under "General Recommendations". This exercise, in addition to providing the usual ammenities of a model, will provide a consistent theoretical and conceptual framework of the leaching process. The resulting perspective and understanding will help to guide future research. Some of the required work is underway. This should be expanded and accelerated to produce early results. Fundamental mechanistic studies are needed to provide input data for such a model. In particular, thermodynamic, kinetic, and hydrologic data on the physical, chemical and biological processes that occur during leaching are needed. Emphasis should be placed on identifying and quantitating fundamental biological and chemical processes.

The resulting models should be used to study different disposal pile configurations and to evaluate potential environmental problems during pile construction. Important differences among side-hill fills, cross-valley fills, and surface piles should be identified and their effect on leachate production and quality assessed. Mine backfilling, proposed by Superior, presents an entirely different problem and has received no public-domain study. Groundwater may leach stowed materials, similar to VMIS retorts.

The models also should be used to investigate leaching problems related to pile construction. Percolation may occur during pile construction, or precipitation events during construction may facilitate subsequent instabilities or percolation. Zones of saturation may form throughout the pile, either from precipitation events that occur during spent shale spreading and compaction or from consolidation of spent shale under load.

Water movement through the piles is one of the most controversial issues today. Early resolution of this problem is required to help guide future work and to facilitate environmentally sound pile design. Moisture profile measurements at existing field sites are needed to assess long-term moisture movement under field conditions. Fundamental hydraulic properties of spent shales, such as unsaturated permeability, should be determined in laboratory studies. The resulting information should be used to help construct a mechanistic model of moisture movement which includes infiltration and runoff of both rainfall and snowmelt. This modeling exercise should be part of the above-discussed water-solute transport model. This model should be validated and used to identify reclamation and design configurations that will retard moisture movement and to assess the environmental impacts of disposal alternatives. The effect of spent shale piles and their leachates on natural recharge should be assessed. The potential for drainage of moisturization water from the base of the pile also should be explored.

In Situ Spent Shale Leachates

Very little realistic work has been conducted on in situ spent shale leachates. Available studies have revealed that in situ leaching is a complex and poorly understood phenomenon, depending on a myriad of hydrologigal, physical, chemical, and other interactions. Recent investigations suggest that the impact of in situ leaching on groundwater quality may be less significant than previously believed. High temperatures and long times at elevated temperatures decrease the solubility of many elements by about an order of magnitude. Aqueous-phase solubility controls may actually improve groundwater quality by providing anions such as sulfate or carbonate which precipitate many toxic metals. Of the elements studied, only V, Pb, and Se may pose an environmental hazard.

Additional work is required to confirm these results and to extend them to include organics and a broader range of conditions. Specifically, additional work in the following areas is recommended:

Characterization

- chemical speciation of inorganics, organics, and organometallics

Field Conditions

- retort cooling
- spent shale temperature when leaching is initiated
- underground sump and bottom plug
- post-retorting reactions between pillars and hot spent shale
- more realistic field simulations
- leach water quality

Mechanisms

- release, transport, and control of pH, TDS, S, V, Pb, Se, Eh
- thermodynamic, kinetic, and hydrologic data for retort and aquifer release release and transport mechanisms

Simulations

- grouting
- intentional leaching
- fracture porosity

Leachate characterization studies have emphasized total organic carbon and elemental concentrations. Assessment of environmental impacts and chemical modeling of the retort-aquifer system will require detailed chemical speciation data, including accurate measurements of Eh and pH. Methods should be developed and used to speciate organics, organometallic, and inorganics in these dilute solutions.

In situ leaching studies have not used experimental conditions that simulate those expected in a commercial process, and they have focused on spent shale isolated from its natural environment. Important field variables, such as porosity, flow rate, initial water temperature, quantity and composition of residual gases, etc., should be specified, and realistic ranges should be determined for each variable. These should be used in future characterization studies.

In situ spent shale leaching studies have focused on the spent shale independent of its natural environment. Several sources of underground contamination exist in field retorts which cannot be properly delineated and evaluated by coring abandoned retorts. These sources/interactions should be studied in the laboratory, using small reactors. Potential post-retorting reactions include those between hot spent shale and retort pillars and mineralogical reactions that occur when water seeps into the retort or which occur during water or gas coolings of the spent shale. Underground sources of contamination include the plug of partially burned material at the bottom of the retort, the underground sump, and shafts and adits. The unburned and partially burned material may contain oil and sorbed organic and metals species, and it may be more leachable than overlying spent shale. The underground sump where the oil-water emulsion is collected, contains residual oily material which is soluble. These interactions and contaminant sources should be studied.

As noted for raw and surface spent shale leachates, fundamental, mechanistic studies are needed to provide input data for geochemical and mass-transfer models so that environmental impacts of leachates may be assessed. In the case of in-situ leachates, such information is required for both the retort and surrounding aquifers. Field studies may be required to obtain the hydrologic data. The resulting models should be used to compare the environmental impacts of an abandoned retort with an identical retort in which grouting or intentional leaching are employed. These models should simulate fracture systems present at the development site.

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TABLE A-1

Summary of Leaching Studies on Green River Raw Oil Shales

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	RAW SHALE SOURCE (Sample Preparation)	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES THAT AFFECT LEACHATE COMPOSITION	STATUS AS OF MARCH 1982
UNIVERSITY OF COLORADO (DOE - R. Franklin)					
• Stollenwerk et al., 1977 Stollenwerk, 1980	Anvil Points, Paraho fines reject, Colony Mine, TOSCO feed (crushed to -65 mesh) Tract C-a Mahogany Zone (screened to -2 mm)	F,B,Mo,As,Se,EC,pH (Complete elemental and ionic analyses for select experiments)	• Shaker (0.4 g/ml; -2 mm) t = 0.25-500 days • Column (3-5 g/ml; -2 mm)	• Solubility as a function of time • Wet-dry cycle • Chemical speciation • Equilibration time • Pore volume	COMPLETE
• Saether, 1980	Anvil Points, Paraho fines reject, Colony Mine, TOSCO feed (crushed to -65 mesh) Tract C-a Mahogany Zone (screened to -2 mm)	F (Complete elemental and ionic analyses for select experiments)	• Shaker (0.05-1 g/ml; -2 mm) t = 1-32 days	• Solid-to-liquid ratio • Ionic strength, pH • Release and uptake mechanisms	COMPLETE
• Runnells and Esmaili, 1981	Anvil Points, TOSCO feed	F,B,Mo,As,Se,EC,pH (Other elements were determined for select experiments)	• Batch (0.4 g/ml; -2 mm) t = 0.25-91 days	• Solubility as a function of time • Leachate interaction with geologic materials • Leachability of surface salt deposits from field lysimeters • Chemical speciation	CONTINUING

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	RAW SHALE SOURCE (Sample Preparation)	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES THAT AFFECT LEACHATE COMPOSITION	STATUS AS OF MARCH 1982
COLORADO STATE UNIVERSITY (EPA - E. Bates)					
• McWhorter, 1980	USBM Horse Draw saline zone, Colony Mine (TOSCO feed) Anvil Points, Paraho fines reject, Tract C-a (two sources)	Al,As,B,Ba,Be,Ca,Cl,CO_3, Cr,Cu,EC,F,Fe,HCO_3,Hg,K, Li,Mg,Mn,Mo,Na,Ni,NO ,Pb, pH,Se,Si,Sn,SO_4,Zn	• Column (3-7 g/ml)	• Saturated and unsaturated conditions • Wet-dry cycle • Pore volume	COMPLETE
(EPA - E. Bates) • McWhorter, 1981b	Tract C-a (run-of-mine), Tract C-b (run-of-mine)	Al,As,B,Ba,Be,Ca,Cl,CO_3, Cr,Cu,EC,F,Fe,HCO_3,Hg,K, Li,Mg,Mn,Mo,Na,Ni,NO_3, Pb,pH,Se,Si,Sn,SO_4,Zn	• Field lysimeters at Tracts C-a and C-b	• Natural weathering conditions	CONTINUING
• Margheim, 1975	Anvil Points	Ca,Cl,HCO_3,K,Mg,Na,SO_4, TDS,pH	• Blender (0.1 g/ml) t = 5 min.	• Composition	COMPLETE
LARAMIE ENERGY TECHNOLOGY CENTER					
• Jackson et al., 1975	Utah	B,Ca,Cl,CO_3,F,HCO_3,K, Mo,Mg,Na,NO_3,Si,SO_4, TDS,TOC,pH	• Blender (0.1 g/ml) t = 5 min.	• Composition	COMPLETE
LAWRENCE BERKELEY LABORATORY (DOE - A. Hartstein)					
• Fox, 1982a	Anvil Points	As species	• Shaker (1 g/ml; -65 mesh)	• Arsenic speciation • Ionic strength	COMPLETE

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	RAW SHALE SOURCE (Sample Preparation)	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES THAT AFFECT LEACHATE COMPOSITION	STATUS AS OF MARCH 1982
LOS ALAMOS SCIENTIFIC LABORATORY (DOE - C. Grua)					
• Peterson, 1981	Tract C-a core, Logan Wash core	Al, As, B, Ba, Ca, Cd, Co, CO_3, Cr, Cu, Cl, EC, F, Fe, HCO_3, K, Li, Mg, Mn, Mo, NO_3, Na, Ni, PO_4, Pb, pH, Si, Sr, SO_4, Se, TOC, Ti, V, W	• Batch (0.2 g/ml; -100 mesh) t = 2 days	• Effect of mineralogy on composition	CONTINUING

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[a] The following abbreviations are used in the Performing Organization column: DOE = Department of Energy; EPA = Environmental Protection Agency.

[b] The following abbreviations are used in the Chemical Species column: EC = electrical conductivity; TDS = total dissolved solids; TOC = total organic carbon.

TABLE A-2

Summary of Surface Spent Shale Leaching Studies

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
UNIVERSITY OF COLORADO (DOE - R. Franklin)					
• Stollenwerk 1980 Stollenwerk and Runnells 1980, 1981	TOSCO II, Paraho	F,B,Mo,As,Se,EC,pH,S (Complete elemental and ionic analyses for select experiments.)	• Shaker (0.4 g/ml; -2 mm); t = 0.25-500 days • Column (2-3 g/ml; -2 mm)	• Solubility as a function of time • Wet-dry cycle • Equilibration time • Chemical speciation • Pore volume • Field validation of laboratory test • Adsorption of S_2O_3 by soil	COMPLETE
• Saether, 1980	TOSCO II, Paraho	F (Complete elemental and ionic analyses for select experiments)	• Shaker (0.02 - 1.0 g/ml; -2 mm); t = 1-32 days)	• Electrophoretic mobility • Ionic strength and pH • Solid-to-liquid ratio • Release and uptake mechanisms • Chemical speciation	COMPLETE
• Glaze, 1981 Glaze and Runnells, 1980	Paraho	F,B,pH,EC,Ca	• Shaker (0.2-1 g/ml; ?); t = 0-280 hrs. • Column	• Particle size, solid-to-liquid ratio, equilibration time • Leachate interaction with local soils	COMPLETE

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
• Runnells and Esmaili 1981, 1982	TOSCO II (fresh)	F,B,Mo,Ca,Li,Sr,EC,pH SO_4,As,Al,Na,HCO_3, Cl	• Shaker (0.4 g/ml; -2 mm); t = 0.25-41 days • Column	• Solubility as a function of time • Solid-to-liquid ratio • Leachate interaction with local soils and geologic materials	CONTINUING
• Brierley and Brierley, 1981	Paraho, TOSCO II	pH,Eh,S_2O_3	• Batch and column (1.1 ml/hr); also, see Stollenwerk, this table	• Microbial S_2O_3 oxidation	CONTINUING
• Klein et al., 1981	?	pH,As	• Batch	• Microbial mobilization of As	CONTINUING
• Caolo et al., 1980 Stanley et al., 1981	TOSCO II, Paraho	Speciation of metal ions and organic ligands; As, Se,Cd,Cr,Pb,Zn,Co,Cu,Ni, Mo	• Ultrasonification (0.05 g/ml) for 2 hrs with CH_2Cl_2 and with water • Columns	• Organic characterization • Effect of moisturization water	CONTINUING
COLORADO STATE UNIVERSITY (EPA - E. Bates)					
• Harbert and Berg, 1978 Harbert et al., 1979 Kilkelly et al., 1981	Paraho, TOSCO II, USBM	pH,EC,Na,Ca,Mg,K,CO_3, HCO_3,NO_3,SO_4,Cl,SAR, sediment	• Field lysimeter	• Location: high elevation (moist) and low elevation (dry) sites • Vegetation • Natural weathering conditions • Soil cover depth and pre-leaching	COMPLETE

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
(LETC - R. Poulson)					
• Ward and Reinecke, 1972	TOSCO II	pH, Na, Ca, Cl, Mg, K, SO_4, HCO_3, EC	• Field lysimeter	• Effect of snowmelt on runoff and percolation composition • Mechanistic leaching and transport model for runoff	COMPLETE
(EPA - F. Pfeffer)					
• Margheim, 1975 Ward et al., 1971	TOSCO II, USBM, Union A	pH, EC, K, Na, Ca, Mg, HCO_3, CO_3, Cl, SO_4, sediment (other constituents were measured in select samples.)	• Batch (0.10 g/ml; -40 mesh); t = 5 min.	• Chemical composition	COMPLETE
			• Column (3 g/ml)	• Chemical composition • Pore volume	
			• Field lysimeter	• Rainfall volume and intensity • Mechanistic leaching and transport model for percolation	
UTAH STATE UNIVERSITY (OWRT - USDI)					
• Maase, 1980 Maase et al., 1980	Union, TOSCO II, Paraho	Polynuclear aromatics	• Soxhlet extraction (0.33 g/ml; -1 mm) with benzene (t = 3 day) followed by methanol (t = 3 day)	• Organic composition, especially PAHs • Effect of chlorine on PAHs	COMPLETE
			• Soxhlet extraction: batch (0.5 g/ml; t = 2-12 hrs) and column using distilled water		

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
(State of Utah, UWRL, USU)					
• Cleave et al. 1979, 1980	Union, Paraho (UT)	Na,Mg,K,Ca,Cl,SO_4, HCO_3, CO_3, TOC,EC,pH, alkalinity (select samples were analyzed for Se, As,Fe,Ba,Pb,Mn,Cu,Zn, Cd,Cr,Ag,B.)	• Shaker (0.1 & 0.2 g/ml); t = 0.5 & 48 hrs • Column (q = 1ℓ /day; $d_{50} \cong 3$ mm)	• Algal bioassays	COMPLETE
(OWRT and State of Utah)					
• Dickson and Adams, 1980 Dickson et al., 1980	Union, Paraho, TOSCO II		• Soxhlet extraction and column; see Maase, 1980 this table.	• Ames test	COMPLETE
(USDA - CSRS)					
• Malek, 1981	Paraho	EC,TDS,pH, sediment	• Field lysimeter • Physical model	• Hydrologic characteristics as a function of volume of rainfall, time interval between applications and surface treatments • Movement and accumulation of salt • Water harvesting techniques	COMPLETE
			• Column	• Effect of compaction and application frequency on quality	

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
(USDA)					
• Fransway, 1980	Paraho	EC,pH,Na,Ca,Mg,K,Cl,SO_4	• Laboratory lysimeter • Batch (0.001 - 1 g/ml); t = 24 hrs	• Effect of particle size and water application rate on water movement and leachate quality • Development of solute transport model • Effect of particle size and solid-to-liquid ratio	COMPLETE
LAWRENCE BERKELEY LABORATORY (DOE - C. Grua/A. Hartstein)					
• Fox, 1982a	Paraho, Lurgi, TOSCO II	As species	• Shaker (1 g/ml)	• As speciation	COMPLETE
LAWRENCE LIVERMORE LABORATORY (DOE - A. Hartstein)					
• Taylor et al., 1982	Laboratory reactor	SO ,Ca,Mg,K,Na,Si,Sr,Al, As,B,Li,Mn,Mo,Pb,V,Zn	• Batch (0.003 - 0.02 g/ml; 200 mesh); t = 24 hrs	• Effect of char oxidation temperature on leachate composition	CONTINUING
BATTELLE PACIFIC NORTHWEST LAB. (DOE - R. Franklin)					
• Garland et al., 1979 Wildung and Zachara 1980, 1981 Wildung et al. 1977-1982 Rogers et al., 1981	Paraho	pH,EC,TOC,DOC,SO_4,S_2O_3, Cl,F,NO_3,NH_4,Si,Na,Ca, Mg,K,Sr,B,Mo,V,Se,As,Zn, Ba,Mn,Cu,Cr,Ni,Li,Fe,Al, U,Sn,Sb (organic speciation on select samples)	• Field Lysimeter	• Natural weathering conditions • Microbial activity • Plant uptake	CONTINUING

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
• Garland et al., 1981 Riley et al., 1981 Wildung et al. 1980, 1981	Paraho	pH,EC,TOC,DOC,SO_4, S_2O_3, Cl,F,NO_3,NO_2,NH_4,Si,Na, Ca,Mg,K,Sr,B,Mo,V,Se,As, Zn,Ba,Mn,Cu,Cr,Ni,Li,Fe, Al,U,Sn,Sb (organic speciation on select samples.)	• Anvil Points and Tract C-a field studies	• Effects of actual disposal operation on hydrologic regime	CONTINUING
• Silviera et al., 1978 Wildung et al. 1979, 1982	Paraho, TOSCO II, Lurgi	pH,EC,Na,Cs,Mg,Sr,K,DOC, TOC	• Shaker (0.1 g/ml; +6.3 mm and -6.3 mm); t = 3 days • Column (3.5 g/ml; -6.3 mm and +6.3 mm)	• Equilibration time • Particle size distribution • Solid-to-liquid ratio • Pore volume • Chemical transport modeling	CONTINUING
DENVER RESEARCH INSTITUTE (NSF - E. Bryan)					
• Schmidt-Collerus et al., 1976 Bonomo, 1974	TOSCO II, USBM	Polynuclear aromatic hydrocarbons	• Soxhlet extraction (0.8 g/ml) with benzene and water; t = 6 days • Field lysimeter	• Organic characterization	COMPLETE
(EPA - T. Powers)					
• Prien et al., 1977 Cotter et al., 1978	Paraho direct and indirect	Polar and polycyclic organic compounds	• Soxhlet extraction (0.8 g/ml) with benzene and water; t = 6 days	• Organic characterization	COMPLETE

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
(USBM)					
• Culbertson et al., 1970	TOSCO	Ca,Na,K,Mg,Al,Fe	• Stepwise batch (0.1 g/ml); t = 2-3 days	• Effect of shale and gasification time and temperature on leachate quality	COMPLETE
COLORADO SCHOOL OF MINES (USBM - Bill Stewart)					
• Farris, 1979	Simulated samples produced in CSMRI differential retort	pH,CO_3,HCO_3,TDS,SO_4,Si Cl,Ca,Mg,Na,K,Fe,Al	• Permeates from ASTM D-243468 permeability test	• Effect of retorting temperature and atmosphere on leachate quality • Effect of moisturization water quality and compactive effort	COMPLETE
UNIVERSITY OF MASSACHUSETTS (NSF)					
• Carpenter, 1978	TOSCO II	Polar and polycyclic organic compounds	• Soxhlet extraction with hexane, benzene, THF, and methanol (0.4 g/ml) for 36-48 hrs and with water (0.3 g/ml) for 48 hrs.	• Organic characterization	COMPLETE
LARAMIE ENERGY TECHNOLOGY CENTER (DOE - A. Hartstein)					
• Jackson and Jackson, 1982	Paraho, Superior	pH,EC,NH_3,TOC,Cl,SO_4,As, Ba,Cd,Cr,Pb,Se,Ag,B,Li, Mn,Mo,Ni,Sr,Th	• Batch: ASTM (0.25 g/ml) and EP toxicity test (0.05 g/ml)	• Effect of retort water codisposal on leachate composition	?

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
COLONY DEVELOPMENT OPERATION					
• Coomes, 1976	TOSCO II	Polycyclic organic compounds	• Not specified	• Organic characterization	COMPLETE
• Metcalf and Eddy, 1975	TOSCO II	Sediment,TDS,pH,Na,K,Ca, Mg,CO_3,HCO_3,Cl,SO_4,$S^=$,Si, Mo,Fe,Al,Cr,Li, moisture content	• Field lysimeter	• Effect of rainfall and snowmelt on quantity and quality of runoff percolation	
			• Blender (2/g/ml); t = 5 min.	• Effect of moisturization water quality	COMPLETE
• Heley, 1976	TOSCO II	pH,EC,moisture content	• Colony embankment	• Moisture movement	COMPLETE
OTHER INDUSTRY STUDIES					
• Holtz, 1976	USBM, Paraho	pH,TDS,Si,Al,Fe,Ca,Mg, Na,K,Li,SO_4,CO_3,HCO_3, Cl	• Shaker (0.1 g/ml); t = 6 hrs.	• Permeability, compactive effort	COMPLETE
			• Column (standard permeability test)	• Effluent recirculation	
		TSS,TDS,pH,oil and grease,SO_4,P,Cl,F,Kjedahl N,Mg,Cu,Fe,K,Pb,Al,Zn,Cd, Mo,Ca,Na,phenols,Si, alkalinity,Hg,CN,$S^=$,B,As	• Field pond	• Compactive effort	
• Fox, 1982b	Paraho	DOC,pH,EC,hydrophobic and hydrologic solutes; acid, base/neutral fraction;N-specific GC	• Compacted core leached as a continuous flow column	• Effect of codisposed gas condensate and retort water on organic composition of leachate	CONTINUING

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
• Union, 1979c	Union B	EC,TDS,TOC,alkalinity, HCO_3,CO_3,Ca,F,Mg,K,Na, SO_4,NH_3,Kjeldahl N,NO_3, NO_2,PO_4,Cl,CN,oil and grease,phenols,$S^=$,Al,As, Ba,Be,B,Cd,Co,Cr,Cu,Fe,Hg, Li,Mn,Mo,Ni,Pb,Se,Sr,V,Zn	• Shaker (0.1 g/ml); t = 5 min.	• Characterization	COMPLETE
• Schmehl and McCaslin, 1973	TOSCO II, USBM	pH,EC,Ca,Mg,Na,K,CO_3, HCO_3,Cl,SO_4	• Batch (saturation extraction) • Column (bulk density = 1.20 g/cm)	• Suitability of samples to support plant growth • Conditions required to remove salt (pore volume, column length)	COMPLETE

[a] The following abbreviations are used in the Performing Organization column: DOE = Department of Energy; EPA = Environmental Protection Agency; LETC = Laramie Energy Technology Center; NSF = National Science Foundation; OWRT = Office of Water Research Technology; USBM = U.S. Bureau of Mines; USDA = U.S. Department of Agriculture; USDI = U.S. Department of Interior; USU = Utah State University; UWRL = Utah Water Research Laboratory.

[b] The following abbreviations are used in the Chemical Species column: DOC = dissolved organic carbon; EC = electrical conductivity; SAR = sodium adsorption ratio; TDS = total dissolved solids; TOC = total organic carbon; TSS = total suspended solids.

TABLE A-3

Summary of Published Laboratory and Field Leaching Studies on In-Situ Spent Shale

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
UNIVERSITY OF COLORADO (DOE - R. Franklin)					
• Stollenwerk, 1980 U.S. DOE, 1980	Occidental - Logan Wash, Core 3E1	pH,EC,F,B,Mo,As,Se,S_2O_3, SO_4,Ca	• Column (2.4-4.3 g/ml) Distilled water (-100 mesh)	• Pore volume • Surface area and charge	COMPLETE
• Meglen and Erickson, 1980	Logan Wash experimental field site	Al,As,B,Ba,BOD,Br,Ca, Cd,Cl,CN,Co,CO_3,COD,Cr, Cu,F,Fe,HCO_3, Hs,K,Li, Mg,Mn,Mo,Na,NH_3,Ni,NO_3, Pb,pH,phenols,PO_4,Sb, Se,S_2O_3,SO_4,$S^=$,Si,Sr, Th,Ti,TOC,V,Zn	• Field study	• Application of statistical methods to identify groundwater impacts	COMPLETE
BATTELLE PACIFIC NORTHWEST LAB. (DOE - R. Franklin)					
• Wildung et al., 1980	Occidental - Logan Wash, Core 3E1	pH,EC,TIC,TC,Al,B,Ca,Cu, Mg,Li,K,Fe,Mo,Mn,Ni,Pb, Si,Sr,Ti,Zn,Zr	• Column (0.9-1.4 g/ml) Distilled water (-100 mesh) q = 0.3-0.4 ml/day	• Pore volume • Air and N_2 atmospheres • Ames test	COMPLETE
LOS ALAMOS SCIENTIFIC LABORATORY (DOE - C. Grua)					
• Peterson et al. 1981, 1982 U.S. DOE, 1980	Occidental - Logan Wash, Cores 3E1, 3E2, 3E3	pH,EC,Al,As,B,Ba,Be,Ca, Cd,Co,Cu,F,Fe,Hg,K,Li,Mg, Mn,Mo,Na,Ni,Pb,Si,Sr,Sn, Se,Tl,Ti,V,W,Zn	• Batch (0.2 g/ml) Distilled water (-100 mesh) t = 2 days	• Solubility as a function of time • Groundwater • Wet-dry cycle • Effect of mineralogy on composition	CONTINUING

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
• Peterson et al., 1982	Laboratory-retorted Colony Mine shale	pH,EC,Al,As,B,Be,Ba,Ca, Co,F,Fe,K,Li,Mg,Mn,Mo,Na, Ni,Pb,Si,Sr,Sn,Se,Ti,V,W, Zn	• Batch (0.2 g/ml) Distilled water (-100 mesh) t = 2 days	• Effect of retorting temperature and atmosphere on composition	CONTINUING
LAWRENCE BERKELEY LABORATORY (DOE - C. Grua/A. Hartstein)					
• Amy, 1978 Amy and Thomas, 1977 Amy et al., 1980	LLL Simulated In-Situ, Anvil Points shale	pH,EC,TOC,organic N, phenols,acid,base and neutral fractions	• Batch (1 g/ml) Distilled water (0.14-0.64 cm) t = 0.5-30 days	• Effect of retorting conditions on composition • Solubility as a function of time • Solid-to-liquid ratio	COMPLETE
			• Column (1.3-2.1 g/ml) Distilled water (0.14-0.64 cm) q = 0.6 ml/min	• Pore volume • Water temperature and quality • Particle size • Flow rate and column length	
• Hall, 1982	LETC 10-ton Simulated In-Situ, Anvil Points shale	pH,EC,TOC	• Column (0.32-2.5 cm) Distilled water	• Evaluate kinetic mechanisms • Effect of media size, velocity, porosity on transfer coefficients • Mechanistic leaching and transport model	COMPLETE
• Fox, 1982a	Occidental - Logan Wash, Core 3E2; LLL Simulated In-Situ	As species	• Shaker (1 g/ml) Distilled water (-100 mesh) t = 48 hrs.	• As speciation • Ionic strength	COMPLETE

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
TEXAS TECH UNIVERSITY (LETC - R. Poulson).					
• Bethea et al., 1981 Parker et al., 1976 Watts, 1977	Laboratory-retorted shale from Colorado and Utah	pH,EC,B,Ca,Cr,Cu,Fe,K, Mg,Mn,Na,Li,SO_4,Sr,Si,Al, Mo,CO_3,Zn,F,Ba,HCO_3	• Shaker (0.2 g/ml) Distilled water t = 15 hrs. • Batch (0.2-0.4 g/ml) Groundwater (3.65 x 5.2 cm core) t = t = 2-21 days	• Effect of temperature (430-1000°C); atmosphere (air, N_2, CO_2); retorting time (15-48 hrs; 23 days) • Groundwater quality and temperature	COMPLETE
LARAMIE ENERGY TECHNOLOGY CENTER					
• Jackson et al., 1975 Virgona et al., 1979	LETC Rock Springs Experimental field site	pH,TDS,Ca,Mg,Na,K,CO_3, HCO_3,SO_4,Cl,NO_3,F,B,Si, TOC;qualitative analysis of major, minor and trace elements by SSMS	• Field study (wells)	• Leachate migration at field site	CONTINUING
	LETC 10-ton Simulated In-Situ	pH,TDS,Ca,Mg,Na,K,B,CO_3, HCO_3,SO_4,Cl,NO_3,F,Si,TOC	• Batch (0.1 g/ml) Distilled water (2.5-3.0 cm) t = 5 min.	• Particle size	COMPLETE
OCCIDENTAL					
• Kuo et al., 1979	Occidental - Logan Wash, Core 3E1	pH,Ca,Mg,Na,K,SO_4,B,As	• Soxhlet extraction (0.05 g/ml) Distilled water	• Characterization	COMPLETE
• Park et al., 1980	Laboratory-retorted shale from Logan Wash	pH,Mg,Si,K,Ca,Na,SO_4	• Batch (0.05 g/ml) Distilled water (-325 mesh) t = 1 hr.	• Effect of retorting (500-1200°C) on composition	COMPLETE

PERFORMING ORGANIZATION[a] (Funding Agency/Program Manager)	SPENT SHALE SOURCE	CHEMICAL SPECIES MEASURED IN LEACHATE[b]	TYPE OF EXPERIMENT (Solid-to-liquid ratio; particle size) t = contact time	SPECIAL STUDIES AND VARIABLES	STATUS AS OF MARCH 1982
COLORADO SCHOOL OF MINES (EPA - R. Newport)					
• Krause et al., 1980	Geokinetics - Seep Ridge site, Utah Samples from retort 1	pH,As,B,EC,F,Mo,SO_4,Se	• Ball Mill Roller (0.40 g/ml) Distilled water (10 mesh) t = 14 days	• Characterization • Effect of retorting conditions	COMPLETE
			• Column, operated in batch mode; Distilled water (-1 m.) t = 1 hr-7 days	• Characterization • Effect of retorting conditions	
U.S. GEOLOGICAL SURVEY (LETC - R. Poulson)					
• Leenheer and Stuber, 1977	Geokinetics - Seep Ridge site, Utah Samples from retort 1	pH,EC	• Column Distilled water q = 2 ml/min	• Effect of retorting conditions	COMPLETE
UTAH STATE UNIVERSITY (State of Utah, UWRL, USU)					
• Cleave et al. 1979, 1980	Geokinetics	pH,Na,Mg,K,Ca,Cl,SO_4, HCO_3, CO_3	• Shaker (0.20 g/ml) Distilled water t = 48 hrs.	• Algal bioassays • Characterization	COMPLETE

[a] The following abbreviations are used in the Performing Organization column: DOE = Department of Energy; EPA = Environmental Protection Agency; LETC = Laramie Energy Technology Center; USU = Utah State University; UWRL = Utah Water Research Laboratory.

[b] The following abbreviations are used in the Chemical Species column: EC = electrical conductivity; SSMS = spark source mass spectrometry; TC = total carbon; TIC = total inorganic carbon; TOC = total organic carbon.

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