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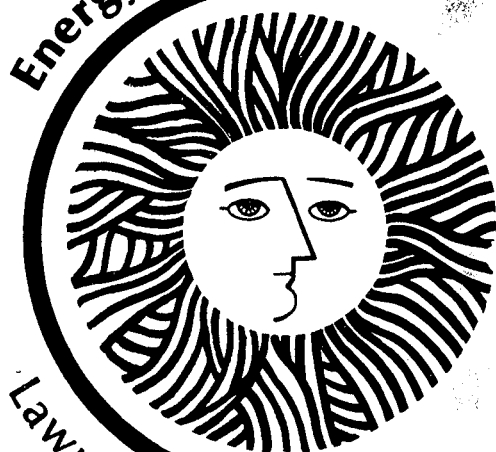
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**A Strategy for the Abandonment  
of Modified In-Situ  
Oil Shale Retorts**

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A STRATEGY FOR THE ABANDONMENT OF MODIFIED  
IN-SITU OIL SHALE RETORTS

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INTRODUCTION

In modified in situ (MIS) oil shale retorting, the resource is processed in the ground. Porosity is introduced into the formation by mining out from 20 to 30% of the in-place oil shale. This material is brought to the surface and either processed in surface retorts or stockpiled. The balance of the material is rubblized underground using various mining techniques. Oil is extracted by pyrolysis and combustion.

This process produces oil, a low BTU gas and process water and leaves behind large underground chambers (retorts) of spent shale and surface piles of raw or spent shale. The acceptability of MIS retorting may depend on the resolution of several environmental issues related to these residuals including groundwater disruption, resource recovery, retort stability and solid and liquid residual disposal.

The purpose of this paper is to investigate the feasibility of returning the solids stockpiled on the surface and process water to the abandoned underground chambers. We believe that potential environmental problems can be largely overcome by returning on-site waste materials to the abandoned underground retort. This would fill the void space created by mining, thus improving structural strength and reducing permeability to groundwater flow. If sufficient strength could be developed, it may be possible to design retorts so that the pillars could be retorted and resource recovery improved. It would also result in the simultaneous disposal of solid and liquid residuals.

CONTROL STRATEGY

Various materials could be introduced into an abandoned retort or surrounding strata to increase structural strength or to reduce the flow of groundwater through the retort. These materials, called grouts, have been widely used in a number of fields including oil field reservoir engineering, nuclear waste containment, gas storage in underground formations, deep coal mining, soil consolidation and various construction activities. The nature of these conventional materials needs to be explored to determine the types of grouts that may be produced from on-site waste materials and properties required for retort sealing.

Any grout used to seal an abandoned MIS retort should have the following characteristics:

- (1) The grouted area must be impermeable enough to prevent the degradation of local ground water or surface water.
- (2) The grouting material must be chemically stable in the presence of saline groundwater.
- (3) The grout viscosity must be low enough and the setting time long enough for the slurry to penetrate a large area.
- (4) The grouted area should be able to withstand both hydrostatic and overburden pressures. The hydrostatic pressure is due to natural head differences that exist between the aquifers surrounding the oil shale deposits in some areas and to significant dewatering during retorting.

An impressive array of commercially-available grouting materials has been used in other industries. These have been extensively described in the literature (1, 2) and include cement and chemical grouts. Cement grouts typically have long setting times, are non-Newtonian and have relatively high viscosities compared to chemical grouts. Chemical grouts are water solutions of various inorganic or organic compounds and are most typically based on sodium silicate, acrylamide, polyphenolic and urea-formaldehydes, lignins, and resins. Properties and cost factors for some of these grouts are compared with spent shale in Table 1. Preliminary estimates indicate that it could cost from 20 to 270 dollars per barrel of oil for the grouting material alone if abandoned retorts were sealed with these conventional materials. Spent shale grouts, on the other hand, may be economically feasible if technical problems associated with their use are resolved.

The high costs of conventional grouts and the on-site availability of some of the raw materials necessary to manufacture them, suggests that waste products be used to produce grouts. Readily available materials include raw and spent shale, latent heat within the retort, gases, process water and mine water. These materials should be considered as raw materials for on-site manufacture of grouts that would not be economically competitive if purchased from commercial sources. Many of these components show promise for use as grouting materials. Some possibilities include on-site conversion of raw or spent shale into a pozzolan or cement, use of  $\text{NH}_3$  in the gas and process water to produce urea-formaldehyde polymers, use of  $\text{CO}_2$  in the gas and  $\text{Na}_2\text{CO}_3$  in the process water to produce insoluble carbonate deposits, and the manufacture of silica gels from mine water, retort waters or offgas.

There are many possible solutions to the retort abandonment problem using these on-site waste products. The most appropriate one will depend on desired strength increase, permeability reduction, retort/aquifer geometry and cost. The following sections of this paper will discuss the use of spent shale and process water as major components of a grout and methods of distributing the grout in the retort.

Table 1. Comparison between conventional grouting materials and spent shale

Class	Example	Viscosity before gelling, cp (range)	Gel time min. (range)	Cost factor relative to neat cement	Potential Application		
					Hydraulic barrier	Provide Struc- tural Strength	
						Medium	High
Cement	Portland cement slurry (neat)	(a)	10-300	1.0	x	x	x
Silicate	Water glass (sodium silicate)	1.5-2	0.1-60	1.3	x	x	x
	Injectrol G (3)						
Polymer	AM-9 polyacrilamde (1)	1.2-1.6	0.1-300	7.0	x	x	x
	PWG (3)	1.5	->300	9.0	x	x	x
Resins	Herculox (3)	13	4-60	4.5	x	x	x
	Epseal (3)	80-90					
Emulsions	Asphalt 65% (4)				x		
Foams	Polyurethane foam (5)		15	1.5	x		
Spent shale	Lurgi (6)	(a)	28 days	0.05			
Lignin base	Blox-All (2)	8-15	3-90	1.65	x		
Unsaturated fatty acid	Polythixon FRD (2)	10-80	25-360		x		
Elemental sulfur		7 cp @ 159 C	sets when cool	available at low cost from gas refining sites			
Formaldehyde base	Urea-formaldehyde (2)	3.5-13	1-60	6.0	x		

(a) Depends on the water-cement ratio (WCR) and presence of additives. With a WCR of 45%, and no additives, the viscosity of neat cement is 200 cp. Addition of a slurry fluidizer (i.e., naphthalene polymer) may reduce this to 20 cp. By comparison, a WCR of 450% to 900% is needed to reduce the viscosity of Lurgi spent shale to 200 cp.

## SPENT SHALE AS A GROUT

Spent shale has been proposed as a grouting material (6) and as a strength-forming material (7). The chemical composition of spent shale is compared with pozzolans in Table 2. This comparison shows that spent shale appears to meet the chemical requirements for ASTM Class C pozzolan and is very similar to natural pozzolans. This is of considerable interest because the spent shale could be used to reduce permeability and provide strength development of an abandoned MIS retort.

Two studies have been conducted on the use of surface spent shale to manufacture a cement-like material. However, these have met with limited success (possibly due to low temperatures reached in the surface retorts). Culbertson, Nevens and Hollingshead (7) studied the stabilization of spent shale from a TOSCO retort. Shear strength and confined compressive strength in the range of 250 to 500 psi were obtained. Strength development was positively correlated with the amount of cohesive hydrates formed. After 15 days of setting, no loss of strength occurred in samples resaturated with water.

Nevens, Habenicht and Culbertson (6) studied the filling of a simulated in-situ retort with a slurry of Lurgi spent shale. Samples calcined at 750 to 850 C required from 500 to 1000 wt % water to reduce the viscosity to 100 cp. Compressive strengths obtained after 28 days ranged from 5 to 200 psi.

Although results with 100% spent shale grouts have been discouraging to date, research is in its infancy and advances may occur. The most promising possibility is to use spent shale to create a hydraulic lime-pozzolan mortar. This is a mixture containing active lime (CaO) and pozzolanically active silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) which yield cohesive hydrates when mixed with water. This strategy is explored here by contrasting the chemistry of cements, pozzolans and mineralogical changes that occur during oil shale retorting.

### Cement, pozzolan and oil shale chemistry

The chemistry of pozzolan and cement and of the carbonate/silicate minerals in oil shale is germane to understanding the potential role of spent shale as a grout. Cements are prepared by blending proper proportions of finely ground limestone and clay and firing the mixture in a kiln at 1450 to 1550 C. The resulting clinker is cooled, about 5% to 6% gypsum is added as a set retarder and the mixture is pulverized. When water is added to this material and the paste is allowed to set it will gradually convert to a hardened product. This process can be represented by the following set of chemical equations:

#### Calcining

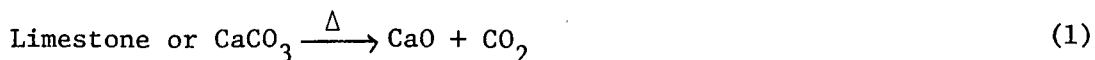
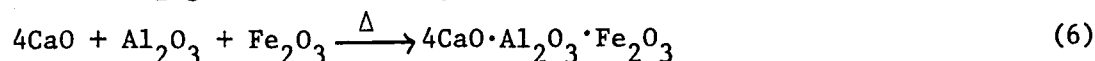
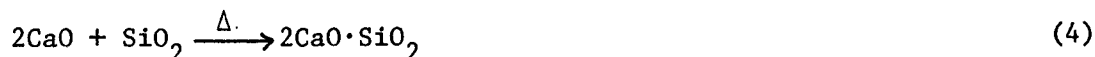


Table 2. Composition of pozzolans and spent shale

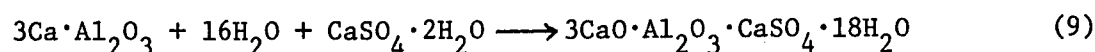
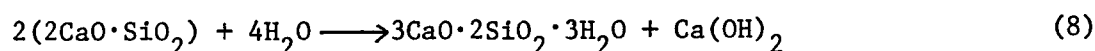
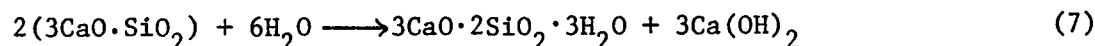
Constituent	Oxide analysis, weight percent				ASTM C-618-78 class C pozzolan
	typical natural pozzolan  (9)	typical industrial pozzolan (lignite fly ash)  (10)	combustion run spent shale		
SiO <sub>2</sub>	55.0	28.7	46.5	)	>50.0
Al <sub>2</sub> O <sub>3</sub>	17.7	12.0	10.7	)	
Fe <sub>2</sub> O <sub>3</sub>	3.5	6.8	4.2	)	
CaO	3.2	40.5	17.2	)	-
MgO	1.0	7.4	7.8		-
SO <sub>3</sub>	-	2.5	-		<5.0
FeO	0.9	-	-		-
K <sub>2</sub> O	6.4	-	3.0		-
Na <sub>2</sub> O	3.4	0.6	3.3		-
Loss on ignition	6.3	0.4	1.6		<6.0



### Formation of Clinker Compounds

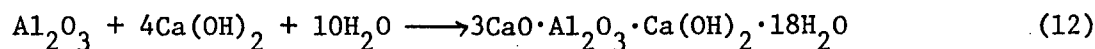
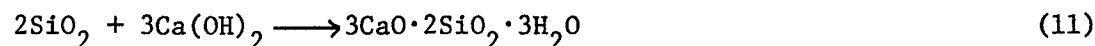


### Hydration



It would not be economically feasible to manufacture cement on site because of the high energy requirements (8). However, a hydraulic lime-pozzolan could be produced at temperatures much below clinkering temperatures.

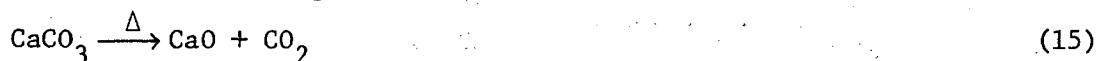
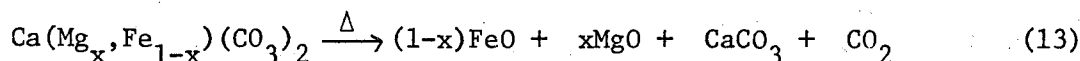
Pozzolans are siliceous and aluminous materials that react with lime in finely divided form and in the presence of moisture to form cohesive hydrates. These hydrates are the main strength-giving compounds of hydrated cement. Typical pozzolanic reactions are:



These equations show that if active silica and alumina react with lime, calcium silicate and calcium aluminate hydrates are formed. These compounds are similar to those that give strength to portland cement. The ability of a siliceous or aluminous material to react at normal temperature as shown is called "pozzolanic activity" and is measured by ASTM Method No. C 311-77 (11). A sufficient degree of pozzolanic activity may be present in spent shale or it may be increased by heat treatment, or by modifying retorting conditions, or by lime addition.

If pozzolanic activity could be induced in surface spent shale by modifying retort operating conditions, it may be possible to manufacture a hydraulic lime-pozzolan on site. This is more attractive than formation of a cement since activation of silica and alumina takes place at lower temperatures than the formation of clinker compounds (900 - 1000 C). For maximum development of cementitious properties, additional lime may be required. This could be added before retorting or afterward. Fine grinding of the spent shale would be required. Because the clinker compounds of portland cement, formed in equations (3) through (6), would not be present, the grout would set more slowly and have a lower final strength.

The feasibility of this strategy depends on the mineralogical changes that occur during the surface retorting process. The effect of oil shale retorting on the mineralogy of spent shale has been studied by Campbell (12, 13). He found that three principal carbonate/silicate reactions occur during oil shale retorting. First, dolomite ( $\text{Ca}(\text{Mg}_x, \text{Fe}_{1-x})(\text{CO}_3)_2$ ) decomposes around 600 C to produce iron and magnesium oxides and calcite ( $\text{CaCO}_3$ ). Calcite decomposes to calcium oxide and carbon dioxide between 700 and 950 C depending on the partial pressure of  $\text{CO}_2$ . Above 1000 C the calcium oxide reacts with silica to produce calcium silicate compounds ( $3\text{CaO} \cdot \text{SiO}_2$ ,  $2\text{CaO} \cdot \text{SiO}_2$ ) and other nonreactive compounds (gehlenites and akermanites). These reactions are summarized as (12):



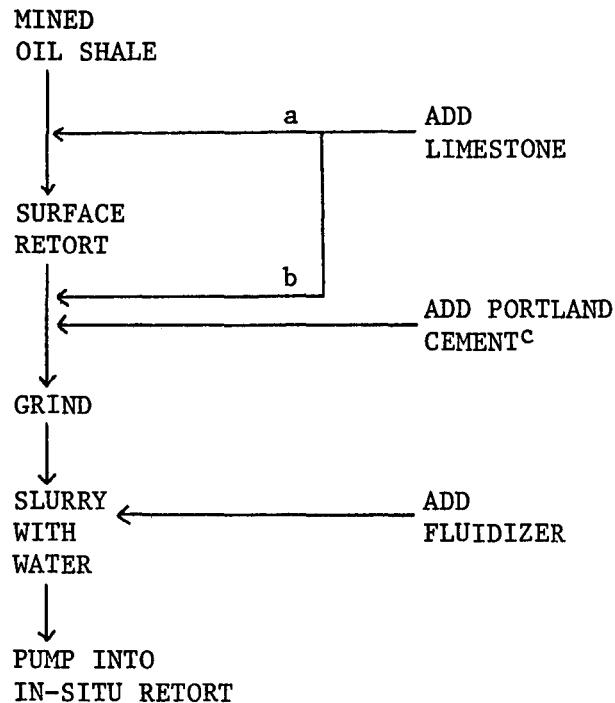
The temperature at which these reactions occur is very important in considering the use of oil shale as a cementitious material. Most surface retorts operate at less than 600 C, which is too low to form a mixture of active silica and active alumina with cementitious properties. Therefore, if spent shale is to be produced for use as a grouting material, the surface retorting process may have to be optimized for pozzolan formation as well as for oil yield.

Based on the foregoing, we propose that the surface retort be operated to produce a hydraulic lime-pozzolan mixture. This recommended strategy is summarized in Figure 1. This figure shows pozzolan production and additives that are being explored in an experimental program. The surface retort is operated to produce a hydraulic lime-pozzolan. The effect of additions of limestone, portland cement and slurry fluidizer are being investigated. The limestone addition would enhance the availability of lime to form cohesive hydrates. If strength of the lime-pozzolan mixture is inadequate, a small addition of portland cement may be desirable. The portland cement would contribute tricalcium ( $3\text{CaO} \cdot \text{SiO}_2$ ) and dicalcium ( $2\text{CaO} \cdot \text{SiO}_2$ ) silicate, which, upon hydration, yield  $\text{Ca}(\text{OH})_2$  and cohesive hydrates. The spent shale pozzolan would react with the  $\text{Ca}(\text{OH})_2$  as it is formed to yield additional cohesive hydrates as shown in equations (11) and (12). The slurry fluidizer would decrease the viscosity of the slurry so that it could be more easily distributed in the abandoned retort.

#### GROUT DISTRIBUTION

Grout distribution in abandoned retorts will depend on several factors including grout properties, retort properties and emplacement geometry. Most commercial grouting is performed by point injection from small diameter pipes placed in a grid pattern on centers less than 20 feet apart. This would not be economically feasible due to the large number of deep holes that would have to be drilled. Well spacing greater than or equal to 70 feet

Figure 1. Recommended strategy for abandonment of MIS retorts



- a Add limestone before retorting if retorting temperature is high enough to calcine limestone.
- b Add calcined limestone after retorting if retorting temperature is not high enough to calcine limestone.
- c Portland cement addition only if strength development without it is inadequate.

would be needed to make grouting attractive as a method of spent shale disposal if drilling were done from the surface. The effects of the geometry of the grout emplacement, the retort permeability and grout viscosity on retort groutability need to be studied.

Viscosity is the most important grout property for distribution. Spent shale slurries investigated to date have typically had viscosities of 500 to over 1000 cp at low water contents (100% by weight water added) (6). These slurries have generally had viscosity reduction to 50 cp at 200% by weight water added but some slurries have required 1000% by weight water to obtain viscosities less than 100 cp (for comparison, the viscosity of water is 1 cp at 20 C). The relative penetrability of spent shale grout will be strongly dependent on obtaining a low viscosity product (< 50 cp) at low water content (100% by weight water) to achieve desired strength development and permeability reduction.

Permeability of the spent in-situ retort will be the most important property for grout distribution. Uniform penetration of a particulate grout (e.g. spent shale-based grout) may be difficult to achieve because of the heterogeneous nature of the void space of an abandoned in-situ retort. It includes large voids between rubble fragments (up to one inch and more), fine voids where oil shale has been fractured but fragments have not moved apart, fissures and cracks in retort walls, and minutes pores created in spent shale by pyrolysis of kerogen. Invasion of only the larger pores may not be adequate to reduce permeability.

Effective grouting may require complete and uniform penetration of most voids. This will be controlled by the relative size of particles in the grout and the void space in the rubble. In order to penetrate a retort at a reasonable pressure and flow rate, the size of the largest suspended particle should not be greater than about one-third of the size of the voids. Typically, particulate grouts are used for openings that are 1/16 inch or larger and chemical grouts are used for openings that are less than 1/16 inch. Therefore, two injections may be required to seal an abandoned in-situ retort. The first would use a grout with a relatively large particle size and the second would use a nonparticulate grout.

Point source grout injection may not be very effective for grout distribution in abandoned retorts. The grout penetration from a point source is severely limited by the high headloss developed near the tip of the pipe. For most commercial grouts however, set up time is short and point sources are used because not enough grout penetration occurs prior to set up for the well point headloss to become a problem. However, for abandoned retorts, this configuration is not suitable as a large number of injection ports would be required. The cost for this may be excessive. Therefore, line source placement should be explored.

Line source injection is beneficial for increased rubble penetration and faster grout distribution but it is limited by the size of the pipe available to deliver the grout and head required to push the grout through the rubble. A 36 inch pipe diameter flowing at 2 ft/sec could deliver 14 cfs of grout to the rubble. If this grout were delivered to a slotted section approximately 50 feet in length, approximately 8 hours would be

required to fill the corresponding 50 foot section of a commercial size retort. Setup time could be important for this approach.

#### SUMMARY

This paper considered the production of a hydraulic lime-pozzolan mixture from spent shale produced in surface oil shale retorts. This mixture could be slurried with process effluents and pumped into abandoned MIS retorts. This control strategy would simultaneously provide for long-term retort stability, minimal groundwater disruption, enhancement of resource recovery and disposal of process residuals. Work completed to date and some theoretical considerations suggest that surface retorts can be operated to produce a spent shale with pozzolanic properties. Additions of limestone, portland cement and slurry fluidizer may be required. Additional work is required to determine optimum retort operating conditions and required additives, and to resolve a number of technical problems. Preliminary cost estimates indicate that this would be an economically viable strategy if technical issues could be resolved. These include high grout viscosities, high water-solid ratios, poor strength development and grout distribution within an abandoned retort. If spent shale grout or some other low-cost on-site waste material cannot be reclaimed for retort filling and plugging, it is possible that MIS retorting may not be both environmentally and economically viable due to the high costs associated with other control strategies. However, if the constraint of enhanced resource recovery is relaxed and if it can be demonstrated that creep and subsidence are not long-term problems, then other lower-cost control strategies may be considered. These would address only the groundwater disruption issues and would include leaching, mine design modifications, grout curtains, and chemical immobilization of leachables.

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