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J. P. Fox

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ABSTRACT

This paper presents the elemental abundances of 47 elements in 23 unfiltered retort waters from three simulated in-situ retorts and of 19 elements in the dissolved and particulate fraction of 11 of these waters. This work indicates that, for most of the unfiltered waters, the carbon, hydrogen, nitrogen, and sulfur occur at concentrations greater than 0.1 percent, that aluminum, arsenic, calcium, iron, potassium, sodium, nickel, and chlorine occur at concentrations greater than 1 ppm, and that all other measured elements occur at concentrations of less than 1 ppm. The particulate fraction in these waters ranges from 203 to 2984 mg/l, and, in most waters, iron, nickel, potassium, and calcium occur at concentrations that are greater than 0.1 mg/l (carbon, hydrogen, nitrogen, and sulfur were not measured in the particulates). All other measured elements (titanium, vanadium, chromium, manganese, gallium, arsenic, selenium, bromine, rubidium, strontium, yttrium, mercury, lead) typically occur at concentrations of less than 0.05 mg/l in the particulates. About one percent of the total elemental mass of potassium, arsenic, and selenium occurs in the particulates while significantly greater than one percent of the elemental mass of iron, chromium, mercury, and nickel may be present as particulate matter. The dissolved metal content of some waters was significantly reduced during filtration by crystallization and bacterial uptake.

Key Words: oil shale, in-situ, retort waters, trace elements, particulates

INTRODUCTION

Oil shales contain organic material in a mineral matrix. The organics are extracted by pyrolysis, producing shale oil, gas, a solid referred to as retorted shale, and an aqueous effluent known as retort water. This may be achieved by using various surface and in-situ retorting processes. In the modified in-situ processes, which are presently of commercial interest, the oil shale is pyrolyzed in the ground following mining of about 20 percent of the in-place material and rubbling of the balance.

This paper discusses the elemental composition of waters produced in laboratory-scale in-situ retorts. This water is coproduced with the shale oil and is referred to here as "retort water." Because the water is produced in closed, pilot-scale retorts designed to simulate an in-situ process, the water is referred to as a "simulated" in-situ retort water. This is an important distinction because differences between simulated retorts and field retorts may affect the chemical composition of the produced water.

Retort water originates from mineral dehydration, steam and moisture in the input gas, the combustion of organics, and groundwater seepage [1]. In closed systems, such as those studied here, only the first three sources are relevant. The amount and composition of these waters depend on shale mineralogy, retort operating conditions, and the design and operation of the product collection system (a condenser system designed to remove oil mist from the gas stream).

Retort waters are produced within the retort as a vapor that is condensed with the oil. Most of the oil and water in a commercial plant will be condensed before the product collection system in an underground sump at the bottom of the retort (process condensate). Entrained oil mist and the balance of the water vapor will be removed at the surface in a condenser

train (gas condensate). The relative proportions and composition of each type of water depend on the exit gas temperature and product collection system design and operation. The process condensate travels down the packed bed of shale in an emulsion with the oil and thus leaches constituents from the shale matrix and from the oil itself. Therefore, this water is expected to contain high concentrations of some elements. The gas condensate, on the other hand, exits the retort as steam and is removed from the gas stream in the condenser train. This water will contain gaseous species not removed at the product sump such as ammonia (NH_3), carbon dioxide (CO_2), hydrogen sulfide (H_2S), some organics, and mercury.

In a commercial in-situ operation, the gas and process condensates may be collected and treated separately due to their different compositions [2]. However, the design and operation of a commercial product collection system have not been investigated, and the effect of such a system on water production and composition has not been studied. In simulated in-situ retorts, these two types of waters have not been distinguished and have generally been combined into a single fraction or only the process condensate has been considered. Additionally, the temperature of the exit gas and the nature of the product collection system have varied significantly from retort to retort. Therefore, the reader is cautioned that the data presented here and elsewhere may not be representative of a commercial in-situ oil shale industry. In this work, the term "retort water" is applied to the aqueous fraction collected from the retort by its operators. The significance of this term as it relates to each retort will be discussed in the experimental and results and discussion sections.

The chemical composition of simulated and other retort waters has been studied by Poulson et al. [3], Jackson et al. [4], Fruchter et al. [5],

Wildeman and Meglen [6], Shendrikar and Faudel [7], Cotter et al. [8], and
Fox et al [9]. These investigations have revealed that retort waters are
brown to yellow in color, have a pH that ranges from 8 to 9, and contain very
high levels of many organic and inorganic constituents. The retort waters
typically have high concentrations (>1000 ppm) of ammonia (NH_3), ammonium
(NH_4), bicarbonate (HCO_3), carbonate (CO_3), sulfate (SO_4), and soluble
organic carbon. The concentration of many elements, with the exception of
nitrogen, carbon, sulfur, hydrogen, sodium, chlorine, iron, potassium,
calcium, arsenic, and nickel, is less than 1 ppm. The organic constituents
are primarily polar and include the normal carboxylic acids and organo-
nitrogen compounds. Few reliable elemental characterizations of these waters
have been obtained due to low elemental concentrations and chemical
interferences [9].

These waters are distinctly different from waters produced by non-energy
industries and other alternate fuel technologies, and are distinguished by
high levels of carboxylic acids, organonitrogen compounds, and oxidized
sulfur compounds such as thiosulfate (S_2O_3). The waters are strongly
buffered by the ammonium bicarbonate (NH_4HCO_3) system, form crystals
during vacuum filtration [10], and support prolific bacterial growth [11].

This paper presents the elemental composition of 15 waters from the
Laramie Energy Technology Center's (LETC) 20-kg controlled-state retort and
eight waters from the Lawrence Livermore Laboratory's (LLL) two simulated
in-situ retorts and discusses the effect of retort operating conditions on
this composition. The morphology and composition of particulates collected
from 11 waters from the LETC retort are also presented.

EXPERIMENTAL

Retorting Systems

Waters from three simulated in-situ retorts -- LETC's 20-kg controlled-state retort and LLL's 125-kg and 6000-kg simulated in-situ retorts -- were studied in this work. These retorts were operated for a range of conditions (Table 1) including temperatures from 494°C (921°F) to 1200°C (2192°F); nitrogen, air and steam atmospheres; isothermal advance rates from 1.3 to 2.6 m/day; shale grades from 40 to 248 litres per tonne; and with shales from Colorado, Utah, Michigan (Antrim), and Morocco.

The LETC controlled-state retort has been previously described by Duvall and Jensen [12] and Bartke and Duvall [13]. Briefly, the retort consists of a 4-m long by 8-cm inside diameter vertical stainless steel tube with a capacity of 20 kg of oil shale. It is fitted at the top with an inlet port for gas and a thermocouple well and at the bottom with a product collection outlet. The tube is surrounded by a continuous series of 24 pairs of 15-cm long electric heaters that are controlled by 24 variable transformers. The product collection system consists of a glass receiver maintained at ambient conditions and two knock-out traps maintained at 0°C (32°F) and -78°C (-108°F). The propagation of a reaction front down a packed bed is simulated by successively turning these heaters on and off. Water and oil are collected in the glass receiver at the bottom of the retort and in the two traps. The water analyzed in this study was collected from the ambient receiver and includes only process condensate.

The controlled-state retort is different in several important ways from field in-situ retorts. These differences may affect the composition of retort waters produced by the two systems. The maximum temperature reached in the controlled-state retort, 760°C (1400°F), is low compared to field

in-situ experiments in which temperatures have reached over 1000°C (1832°F). These higher temperatures may result in a greater distribution of elemental mass from the raw shale to the retort water than observed here. In the controlled-state retort, the reaction zone consists of a pyrolysis zone, and heat for pyrolysis is supplied by external electric heaters. The reaction zone in field retorts consists of a pyrolysis zone and a combustion zone, and heat for pyrolysis is derived from the trailing combustion zone. Therefore, the retorting atmosphere in the controlled-state retort is reducing while in field retorts, both oxidizing and reducing conditions may occur. The particle size ranges studied here are much smaller and the void fraction much higher than those anticipated for field retorts. Significant differences may also exist between the product collection system used in the controlled-state retort and in a commercial operation. The retort water analyzed here consists only of process condensate collected under ambient conditions while in field retorts process condensates may be collected at higher temperatures.

Lawrence Livermore Laboratory (LLL) operates two pilot-scale simulated in-situ retorts. These systems have been previously described by Sandholtz and Ackerman [14] and Raley et al. [15]. The smaller retort is 0.30 m in diameter by 1.5 m high and has a capacity of 125 kg of oil shale. The larger retort is 0.91 m in diameter by 6.1 m high and has a capacity of 6,000 kg of oil shale. Both retorts are surrounded by a contiguous series of 15 cm vertical electrical-resistance heaters to prevent the loss of process-derived heat through the retort walls. The retorts are fitted at the top with an inlet gas port and a thermocouple well and at the bottom with a product collection system.

The retort water from the smaller retort (designated by the letter "S") consisted of a composite of waters collected from the oil-water receiver at the bottom of the retort and from a series of condensers maintained at 15°C (59°F), 5°C (41°F) and -5°C (23°F). Therefore, the S-series waters are a mixture of process and gas condensates. The retort water collected from the larger retort (designated by the letter "L") was obtained only from the receiver at the bottom of the retort and corresponds to process condensate.

These retorts are believed to simulate closely a field retort. They support combustion, and the vessels are nearly adiabatic. The principal differences between these retorts and a field retort are the small particle size range, the high void fraction used, and the product collection system.

Sample Preparation

The dissolved and particulate fractions of 11 waters were analyzed for 19 elements and 23 unfiltered waters were analyzed for 47 elements. All waters were stored in polyethylene containers at less than 4°C (39°F). They were not acidified to eliminate the formation of a precipitate.[9]. Because the waters were very heterogeneous, they were constantly agitated during the removal of aliquots. This was accomplished by placing a small Teflon stir bar in the bottom of each container and placing the container on a magnetic stirrer during sampling.

Eleven of the waters were filtered through a Millipore type HA 0.45 μm filter paper under vacuum at a rate of about 1 ml/sec. A sample volume sufficient to give a particulate unit mass of about 1 mg/cm^2 (5 to 25 ml) was filtered and the filtrate transferred to a polyethylene container. The filter paper was dried under silica gel and weighed daily until a constant weight within two percent was obtained. The abundance of 17 elements in the

filtrate and the particulate fraction was determined by x-ray fluorescence

spectrometry and Zeeman atomic absorption spectroscopy (for mercury).

Analytical Methods

The 23 unfiltered waters studied here were analyzed for 47 elements using

neutron activation analysis, x-ray fluorescence spectrometry, and Zeeman

atomic absorption spectroscopy. The 11 filtered waters and their particulate

fractions were analyzed for 19 elements using x-ray fluorescence spectrometry

and Zeeman atomic absorption spectroscopy. Particulate morphology was

studied by scanning electron microscopy. The accuracy of the techniques used

was validated by analyzing the standard, Omega-9 [9], and by interinstru-

mental and interlaboratory comparisons.

Neutron Activation Analysis—Most of the unfiltered retort waters were

analyzed at Lawrence Livermore Laboratory (LLL) by an absolute instrumental

neutron activation technique described elsewhere [16]. Samples CS-72, CS-73,

and CS-74 were not analyzed by neutron activation analysis due to inadequate

sample; and samples S-9, S-10, and S-11 were analyzed early in the study by a

calibration technique to be described subsequently. In the absolute

technique, approximately 10 ml of water were spiked with 0.26 µg scandium and

evaporated in a Teflon beaker at 50°C (122°F) to 60°C (140°F) onto 200 mg of.

Avicel (microcrystalline cellulose). The dried residue was pressed into

1.6-cm-diameter disks for irradiation and counting. The technique used two

irradiations and five decay/counting sequences. The samples were counted on

20- to 70-cc Ge(Li) detectors. The samples were first irradiated for

30 seconds at a flux of 2.2 x 10^{13} n/cm^2-sec followed by a 10 minute

decay and 10, 20, and 40 minute counts during which aluminum, vanadium,

copper, titanium, calcium, sodium, magnesium, chlorine, manganese, bromine,

iodine, barium, indium, dysprosium, arsenic, gallium, samarium, and

molybdenum were measured. The samples were then irradiated for 72 minutes at a flux of 2.5 x 10^{13} n/cm^2-sec followed by a 3-day decay and a 133-minute count during which sodium, arsenic, tungsten, gallium, potassium, cadmium, molybdenum, vanadium, samarium, gold, mercury, lanthanum, antimony, and zinc were measured; and a 15-day decay followed by a 333-minute count during which iron, chromium, cobalt, zinc, mercury, selenium, silver, antimony, cerium, cesium, europium, scandium, thorium, nickel, tantalum, hafnium, barium, and rubidium were measured.

Unfiltered retort water samples S-9, S-10, and S-11 were analyzed by a calibration method of neutron activation analysis at Battelle Pacific Northwest Laboratories (PNL). Approximately 4 ml of sample were pipetted into 2-dram polyethylene vials, and the vials were heat sealed. To minimize any possible leakage in the reactor, the samples were placed within two additional containers -- a plastic bag and a 4-dram polyethylene vial -- each of which was heat sealed. The samples and standards were stacked singly in dry tubes of the Lazy Susan of Oregon State's TRIGA reactor. Standards used were Fischer atomic absorption standards for arsenic, nickel, zinc, and selenium; National Bureau of Standards (NBS) orchard leaves (SRM 1571); U. S. Geological Survey standard rocks AGV-1, PCC-1, and W-1; International Atomic Energy Agency Standard (IAEA) Soil-5; and a standard Columbia River basalt.

The technique used to analyze these samples and standards consisted of a single irradiation and three decay/counting measurements. The samples were irradiated for 2 hours at a flux of 6 x 10^{12} and counted for 30, 300, and 300 minutes following cooling periods of 3 days, 3 weeks, and 6 weeks, respectively. Following the irradiation, the samples were removed from their packaging with a syringe and transferred to a 20-ml polyethylene vial for counting. The samples were counted on an 80-cc Ge(Li) detector with a

resolution of 1.96 keV at 12 percent relative efficiency after the 3-day and 3-week cooling periods. Counting following the 6-week cooling period was done on an anticoincidence-shielded Ge(Li) detector to reduce Compton background for low- and medium-energy gamma rays, and, in some cases, to remove peak interferences from correlated gammas. The elements sodium, lanthanum, samarium, uranium, lutetium, arsenic, potassium, calcium, and bromine were measured following the 3-day cooling period in a 30-minute count. The elements antimony, cobalt, iron, rubidium, scandium, barium, hafnium, chromium, thorium, and europium were measured following the 3-week cooling period in a 300-minute count, and the elements strontium, nickel, rubidium, zinc, and selenium were measured following the 6-week cooling period in a second 300-minute count.

X-ray Fluorescence Spectrometry—Energy dispersive x-ray fluorescence spectrometry (XRF) was used to measure titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, arsenic, selenium, bromine, rubidium, strontium, yttrium, lead, and thorium in unfiltered retort waters and potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, gallium, mercury, arsenic, lead, selenium, bromine, rubidium, strontium, and yttrium in filtered retort waters and particulates. The instrumental technique is described elsewhere [17]. The system used consisted of a prototype energy-dispersive x-ray fluorescence spectrometer designed and built at Lawrence Berkeley Laboratory (LBL). The total system resolution full width at half maximum (FWHM) was 190 eV at 6.4 keV (Fe Kα x-ray) at 5000 counts/sec using 18 μsec pulse peaking time. Excitation was provided by a molybdenum x-ray tube with external molybdenum filters. The x-ray tube was operated at 45 keV and regulated currents varying from 100 to 245 μA. The resulting x-rays were simultaneously

measured by a guard-ring detector with pulsed-light feedback electronics and a 512-channel pulse-height analyzer.

Unfiltered retort water was analyzed by pipetting 0.5 ml of sample into an XRF liquid cell and directly analyzing the liquid. Filtered retort waters were prepared by pipetting seven 4-μl drops of sample onto a 0.006-mm polypropylene film tightly stretched in a plastic ring. Drop location was controlled with a jig designed to produce seven concentric spots. These deposits were air dried and the samples counted for 2000 sec.

Particulates were analyzed directly on the filter paper. Disks 2.5 cm in diameter were cut from the paper containing particulate deposits and analyzed as described above. Blank corrections were made. The samples were counted for 20 or 40 min.

Zeeman Atomic Absorption Spectroscopy—This technique was used to measure mercury and cadmium in the unfiltered and filtered retort waters and mercury in the particulate phase. The technique is described elsewhere [18,19]. The waters were analyzed by directly pipetting the sample into either a platinum boat (mercury) or directly onto a graphite rod (cadmium). Spike recoveries and standard additions were used for all samples. Standards were prepared daily in a one percent nitric acid (HNO_3) matrix from 1000 ppm stock solutions. The particulates were analyzed by punching small diameter circles from the filter paper with a single-hole paper punch and directly inserting these disks into the furnace on a platinum probe.

Chemical Methods—Total carbon, total hydrogen, and total nitrogen were determined on a Carlo Erba Model 1104 elemental analyzer gas chromatograph. A sample of about 2 mg was combusted in 10 ml of pure oxygen (O_2) and swept through a Pora-Pak Q column. Elemental nitrogen, CO_2 and water (H_2O)

were detected and the peaks integrated. Calculations were made with factors determined from standards obtained from the National Bureau of Standards.

Inorganic carbon was determined by reacting a sample of about 100 mg with 20 percent perchloric acid ($HClO_4$) and evolving CO_2. The CO_2 was swept into a coulometric titrator. Organic carbon was calculated by subtracting inorganic carbon from total carbon.

Total sulfur was determined by combusting a sample of about 100 to 200 mg in an O_2 atmosphere. The sulfur dioxide (SO_2) formed was titrated automatically with potassium iodate (KIO_3). Factors used in this determination were calculated using standards.

Scanning Electron Microscopy (SEM)—This technique was used to examine and analyze the particulates collected from oil shale retort waters. The SEM system used in this work was an Advanced Metals Research Model 1000 A operated with a 20 keV electron beam excitation potential. The SEM was equipped with an energy-dispersive analyzer x-ray (EDAX) Model 711 x-ray fluorescence analyzer. The XRF system scanned the energy spectrum from 0 to 8 keV at incoming count rates of 100 to 1000 counts/sec.

RESULTS AND DISCUSSION

Unfiltered Retort Waters

The elemental abundances measured in this study for retort waters produced by simulated in-situ retorting of Green River, Antrim, and Moroccan oil shales are summarized in Table 2 and compared with abundances reported elsewhere for other simulated in-situ retorts and for two field experiments. This table indicates that the major constituents (>0.1 percent) in these waters are carbon, hydrogen, nitrogen, and sulfur. (Although hydrogen is not reported, it is a minimum of 11.1 percent by weight in the water). The elements aluminum, arsenic, calcium, iron, potassium, sodium, nickel, and

chlorine occur at greater than 1 ppm while all other elements occur at concentrations that are less than one ppm.

Table 2 also compares the abundances measured in this study with those measured in retort waters from other simulated in-situ retorts and from field experiments. The comparison with field results is particularly pertinent as it indicates how reliably laboratory data may be extrapolated to larger scale field experiments. This comparison indicates that the elemental abundances in Green River retort waters measured in this study are consistent within an order of magnitude with those for other simulated retorts, and for field experiments for all elements except mercury, molybdenum, and sodium. The mercury levels are lower and the sodium levels are higher in waters from the field experiments than in waters from simulated retorts, and molybdenum is higher in Geokinetics water than in the others. The high sodium levels in waters from the field experiments are probably due to groundwater intrusion into the burn area or to the presence of nahcolite ($NaHCO_3$) in the retorted formation.

Table 2 also indicates that there is a large range in the Green River retort water elemental abundances measured here. The ratio of the maximum to the minimum value reported in column 2 ranges from 1.3 for aluminum to 582 for sodium and averages 75. This is consistent with the variability noted by others [3,4] and is hypothesized to be due to sampling and between-run and between-retort variation in product collection system operation. The composition of these waters depends, among other things, on the contact time between the oil and water (variable depending on sampling strategy), on the residence time of the water within the retort (contact time between shale, gas, and water), and on the operation of the product collection system. Since these variables were not controlled here nor in other work, it is

hypothesized that they may be responsible for the large variations in retort waters. The detailed elemental abundances in each of the unfiltered waters studied here are presented in Tables 3 (LETC samples) and 4 (LLL samples). Corresponding elemental abundances in raw and spent oil shales and shale oils are reported by Fox [21]. An analysis of the data in Tables 3 and 4 indicates that shale source, retort, temperature, and input gas had a significant effect on retort water composition for some elements.

The elemental composition of the raw and spent oil shale did not significantly affect the elemental composition of produced water for most elements, and there is no statistically significant difference in the elemental composition of Green River, Antrim, and Moroccan retort waters, with a few exceptions. Uranium is significantly higher, and manganese, lanthanum, cobalt, sodium, and chromium are significantly lower in both Antrim and Moroccan retort waters than in most Green River waters. The cobalt, sodium, and lanthanum are also significantly lower in Antrim and Moroccan oils than in Green River oils [21], which suggests that they may migrate together or originate from the same source. Sodium is significantly lower in the Antrim and Moroccan shales than in the Green River shales [21].

In addition to these differences, molybdenum and potassium are significantly higher in Antrim and selenium in Moroccan retort waters than in the other retort waters, while cesium is lower in Moroccan waters than in the others. The elevated selenium concentration in the Moroccan waters is consistent with elevated selenium concentrations in the Moroccan shale oil and original shale [21]. The only significant difference between retort waters produced from the Utah and Colorado shales studied here is that the sodium concentration is significantly lower in waters from the Utah shales than in waters from the Colorado shales. This is consistent with results reported by

Jackson et al. [4] who hypothesized that it is due to the relatively higher amounts of nahcolite in oil shales from the Piceance Creek Basin of Colorado than in oil shales from Utah.

The only retort operating conditions that had a significant effect on the elemental composition of retort waters were temperature and input gas. These parameters affected the concentrations of nitrogen, lanthanum, antimony, arsenic, and organic carbon in the retort waters studied here. The lack of other clear relationships may be due to sampling problems or uncontrolled variables such as contact time between the oil and water, handling and storage of samples, and operation of the product collection system. This is consistent with observations of other investigators who similarly found no relationship between retorting conditions and water composition [3,4].

There were also some significant differences between waters produced by the two retort systems studied here. These differences could be due to some combination of operating conditions and other factors. There were not enough data to separate the effect of retort operating conditions and other factors, such as operation of the product collection system or contamination. These between-retort differences will be discussed following the discussion of individual elements.

Inorganic Carbon. Retorting temperature and input gas had a significant effect on the concentration of inorganic carbon in the retort waters. The concentration of inorganic carbon was directly related to temperature in the nitrogen runs, and steam increased the inorganic carbon concentration in the LETC waters and decreased it in the LLL waters (The decrease in inorganic carbon during steam runs in the LLL retorts is due to dilution from excess steam and will be discussed below under "Minor and Trace Elements").

The majority of the CO_2 is produced by carbonate decomposition, which starts at about 400°C and increases up to about 950°C. This accounts for the direct dependence of inorganic carbon on temperature. The increase in inorganic carbon in steam runs is probably due to the reaction of carbon monoxide (CO) with steam to produce CO_2 and hydrogen (H_2).

Nitrogen. The nitrogen concentrations are significantly higher in retort waters produced in N_2/steam/O_2 atmospheres at 760°C than in waters produced under other retorting conditions. There is inadequate data to determine whether the elevated nitrogen levels are due to the higher temperature or the atmosphere. It is, however, hypothesized that it is due more to the temperature than the input gas. The higher temperature would decompose more of the nitrogen compounds in the oil shale, making more gaseous nitrogen available for dissolution in the water.

Minor and trace elements. The lanthanum, antimony, and arsenic were considerably lower in steam runs of the LLL retorts than in most other runs. This is also true for inorganic carbon, as noted previously. This trend does not occur for steam runs of the LETC retort. In the LETC retort runs, 0.04 gm steam were added to the system for each gm of shale retorted while, in the LLL runs, 0.17 gm steam were added for each gm of shale retorted. The four-fold excess of steam used in the LLL runs may have diluted the lanthanum, antimony, arsenic, and inorganic carbon or inhibited their mobility. The arsenic appears to be merely diluted by the steam as the dilution factor computed from mass balance data (6.1) is comparable to the ratio of arsenic in non-steam to steam runs (6.4). However, the ratio of lanthanum and antimony in non-steam to steam runs is significantly greater than 6.1, suggesting that steam may inhibit the mobility of these elements. On the other hand, the ratio of 3.2 of inorganic carbon in non-steam to steam runs suggests a combination of dilution and excess CO_2 production.

The most striking differences in elemental abundances occur between the two retort systems studied. The lanthanum, antimony, arsenic, cobalt, sodium, nickel, and rubidium are significantly lower and the cadmium, chromium, and copper significantly higher in waters from the LLL retorts than in those from the LETC retort. Because of the scatter in the data, other trends were not identified. These differences may be due to retort operating conditions or to the product collection system design and operation. The LLL retorts use a larger sized shale, support direct combustion, and employ a radically different product collection system. The LETC waters consist primarily of process condensate while the LLL waters, with the exception of L-1, consist of both process and gas condensates.

The elevated levels of copper and chromium in the LLL waters are hypothesized to be due to contamination from the retorting system. The high temperatures and the corrosive gas atmosphere due to the presence of hydrogen sulfide (H_2S) within the system may have mobilized constituents from the metal surfaces. The data in Table 4 indicate that there were high levels of zinc, copper, and iron in waters from runs S-10 and S-11. Conversations with the retort operators implicated the alloys used in the product-collection system. This situation was improved in subsequent runs. The cause for the lower concentrations of lanthanum, arsenic, antimony, cobalt, sodium, nickel, and rubidium in LLL waters than in LETC waters is unknown.

Retort Water Particulates

Eleven retort waters from LETC's controlled-state retort were filtered, and the particulate fraction and the filtered water collected and analyzed for 19 elements by energy-dispersive x-ray fluorescence spectrometry (XRF). The elemental composition of the particulates and the filtered waters and the percent of the total elemental mass associated with the particulates are

summarized in Table 5. Two of the measured elements, copper and zinc, are not reported due to contamination problems. This summary shows that the major elements (>0.1 mg/l) in the particulate fraction are iron, nickel, potassium, and calcium. All other measured constituents typically occur at less than 0.05 mg/l. The fraction of the total elemental mass present in the particulates (percent particulate) is typically less than, or about, one percent for potassium, arsenic, and selenium. The percent particulate is significantly greater than one percent for iron, chromium, mercury, and nickel in most samples.

The morphology and chemical composition of individual particles present in the particulate fraction of three waters are presented in Figs. 1-3. These figures are scanning electron micrographs of particulates from representative waters and x-ray spectra of individual particles shown in the micrographs. Since only a small area is represented by each micrograph, it should not be assumed that the types of particles present are limited to those shown.

A visual classification of the particles revealed that there were two types present: crystals and amorphous solids. These particles are imbedded in a uniform background of spongy or scaly material. The only element detected in the matte material was sulfur (carbon and nitrogen are likely to be present but cannot be detected by EDAX). The amorphous particles were rounded (see Fig. 3) and their chemical composition is silicon-aluminum-(calcium, potassium, iron, sodium). These particles are hypothesized to be spent shale particles. The crystalline particles were varied in shape and are composed of iron, calcium, magnesium or nickel (Figs. 1 and 2). The particles range in size from a micron or less to about 100 μm and are hypothesized to form during vacuum filtration of the sample.

ACKNOWLEDGEMENTS

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Table 1--Retort operating conditions.

Run	Shale type	Shale grade (litre/ tonne)	Shale size range (mm)	Oil yield, % Fischer assay (volume basis)	Isothermal advance rate (m/day)	Maximum centerline temperature (°C)	Sweep gas	Gas flow rate, standard (m^3/m^2-min)
LETC CONTROLLED-STATE RETORT								
CS-60	Colorado[a]	123	3-13	46	1.8	540	N_2	0.12
CS-61	Colorado	88	3-13	92	1.8	540	N_2	0.12
CS-62	Utah	126	3-13	95	1.8	540	N_2	0.12
CS-63	Antrim	40	3-13	77	1.8	540	N_2	0.12
CS-64	Colorado	248	3-13	94	1.8	540	N_2	0.12
CS-65	Moroccan	79	3-13	88	1.8	540	N_2	0.12
CS-66	Colorado	128	3-13	91	1.8	540	N_2 + steam	0.15
CS-67	Colorado	231	3-13	100	1.8	540	N_2 + steam	0.15
CS-68	Colorado	119	3-13	97	1.8	540	N_2	0.12
CS-69	Colorado	118	3-13	98	1.8	760	N_2 + steam + O_2	0.15
CS-70	Colorado	134	3-13	96	1.8	540	N_2 + steam	0.15
CS-71	Utah	137	3-13	91	1.8	540	N_2 + steam	0.15
CS-72	Colorado	89	3-13	97	1.8	540	N_2 + steam	0.15
CS-73	Moroccan	77	3-13	97	1.8	540	N_2 + steam	0.15
CS-74	Colorado	82	3-13	102	1.8	760	N_2 + steam + O_2	0.15
LLL RETORTS								
S-9	Colorado	100	13-25	98	1.4	494	N_2	1.06
S-10	Colorado	100	13-25	95	1.3	868	Air + recycle	0.64
S-11	Colorado	100	13-25	92	2.6	1003	Air	0.61
S-12	Colorado	100	0.001-76	93	2.1	942	Air + N_2	1.14
S-13	Colorado	100	13-25	96	2.2	887	Air + steam	0.72
S-14	Colorado	100	0.001-76	88	1.6	1010	Air + steam	0.7
S-15	Colorado	84	0.001-25	86	1.5	1025	Air + steam	0.7
L-1	Colorado	107	0-76 + blocks	75	1.7	900-1200	Air + N_2	1.1

CS = controlled-state retort; S = LLL 125-kg retort; L = LLL 6000-kg retort.

[a]This is an interrupted run in which only half of the charge was retorted (see Ref. 10).

Table 2. Comparison of elemental abundances in retort waters measured in this study with those measured in waters from other simulated in-situ retorts and two true in-situ field experiments (in ppm).

	Unfiltered retort waters measured in this study				Measured in other studies		
	Shale Type				Other simulated in situ retorts[a] (unfiltered)	True in situ, Site 9[a] (filtered)	True in situ, Geokinetics[b] (unfiltered)
	Green River		Antrim	Moroccan			
Element	Average	Range					
Al	--	12.5-16.4	—	—	0.041-16.6	<003-19.1	--
As	4.5	0.284-15.3	1.83	2.5	1.8	1.0	2.55
Ba	0.30	0.097-0.57	--	--	0.07	0.71	0.54
Br	0.19	0.038-0.53	0.37	0.35	0.082	2.4	0.18
C(org),%	0.35	0.20-0.56	0.17	0.58	0.47	0.10	--
C(inorg),%	0.86	0.33-1.76	0.22	0.26	0.75	0.33	--
Ca	16	6-26	14	9	7.6	12	33
Cd	0.01	0.00069-0.054	0.0065	0.0089	<0.001-0.005	0.0016	0.084
Ce	0.01	0.0037-0.027	0.014	<0.011	--	<0.026	--
Cl	365	11-1175	387	346	0.007-1910	824	3016
Co	0.32	0.031-0.643	0.027	0.020	0.12	0.030	0.56
Cr	0.45	0.028-1.40	0.09	0.009	0.015	0.02	0.078
Cs	0.032	0.0056-0.066	0.081	0.005	--	0.0021	--
Cu	--	<0.09-139	0.35	0.19	0.019	0.10	0.21
Eu	--	<0.00008-0.0002	<0.0002	<0.0002	--	<0.0013	--
Fe	7.7	1.21-27.2	2.7	2.0	7.6	1.2	14.0
Ga	0.05	<0.06-0.013	0.06	0.07	--	0.004	--
Ge	--	<0.06-0.13	0.05	0.15	--	0.013	0.044
Hf	0.0028	0.0014-0.0049	0.0048	--	--	0.015	--
Hg	0.08	<0.0005-0.196	0.080	0.32	<0.001-0.39	0.0003-0.021	0.004
I	0.16	0.13-0.25	0.15	0.41	<0.001-1.3	0.59	--
K	23	<4-54	163	60	37	47	121
La	0.03	0.00025-0.12	0.008	0.003	--	0.006	--
Mg	--	<3.1-<39	29	24	22	20	17
Mn	0.23	0.0022-0.39	<0.02	<0.02	0.099	0.09	0.94
Mo	0.47	0.010-1.39	2.84	0.29	0.033-1.2	0.60	12
N,%	1.69	1.00-2.97	1.13	1.04	--	--	--
Na	621	3.06-1780	193	197	320	4333	9392
Ni	2.45	0.24-10.7	1.0	2.6	0.014-2.6	0.06	1.62
Pb	--	<0.24-1.15	<0.24	<0.24	0.002-0.83	0.0045-0.02	0.64
Rb	0.36	0.019-0.80	1.21	0.34	--	0.16	--
S,%	0.17	0.05-0.85	1.15	0.76	0.001-0.23	0.20	--
Sb	0.20	0.0033-1.10	0.92	0.36	--	1.9	0.011
Se	0.64	0.228-1.42	0.44	6.5	<0.001-1.7	0.21	0.22
Sm	--	0.00006-0.0017	--	0.0015	--	<0.0013	--
Sr	0.4	0.10-0.91	0.37	0.12	--	1.12	0.002
Ta	--	0.0056-0.051	--	0.013	--	0.045	--
Th	0.0038	0.0008-0.0094	0.17	<0.18	--	0.0037	--
Ti	--	<0.57-2.7	0.69	<0.60	--	<0.02-2	--
U	0.062	0.0011-0.195	0.73	0.28	0.018-93	0.55	--
V	--	0.023-0.19	<0.06	<0.04	0.27	0.12	0.43
W	0.06	0.0057-0.13	--	--	--	0.010	--
Y	--	<0.15-0.8	<0.15	<0.15	--	0.001	--
Yb	0.0014	0.00094-0.0021	--	--	--	<0.002	--
Zn	1.8	0.09-13.3	0.92	0.85	0.28	0.31	0.095

[a] See Ref. 9.
[b] See Ref. 20.

Table 3. Concentration of major, minor, and trace elements in unfiltered retort waters from the LETC controlled-state retort, rms CS-60 through CS-67 (in ppm except as noted).

Element	CS-60	CS-61	CS-62	CS-63	CS-64	CS-65	CS-66	CS-67	Element
Al	-	-	-	-	-	-	-	-	Al
As	6.35±0.45	4.20±0.03	6.93±1.23	1.83±0.07	3.79±0.43	2.48±0.12	12.0 ±1.6	3.43±0.31	As
Ba	-	-	-	-	-	-	0.23±0.18	0.14±0.12	Ba
Br	0.07±0.02	0.23±0.01	0.10±0.01	0.37±0.01	0.30±0.01	0.35±0.01	0.073±0.013	0.21±0.01	Br
C(org),%	0.43±0.06	0.37±0.01	0.36±0.01	0.17±0.01	0.34±0.01	0.53±0.01	0.43±0.01	0.43±0.01	C(org),%
C(inorg),%	0.66	0.83±0.01	0.62±0.01	0.22±0.01	0.56±0.01	0.16±0.01	0.86±0.01	0.55±0.01	C(inorg),%
Ca	26±1	-	6±1	14±1	14±1	9±1	23±1	6±1	Ca
Cd	0.0038±0.0005	-	0.0058±0.0048	0.0065±0.0008	0.0012±0.0004	0.0089±0.0002	0.004±0.006	0.00069±0.00045	Cd
Ce	<0.020	<0.008	0.004±0.003	0.014±0.006	0.014±0.004	<0.011	0.008±0.003	<0.011	Ce
Cl	1175±11	359±4	353±3	387±6	372±5	346±3	271±5	326±4	Cl
Co	0.385±0.004	0.313±0.002	0.421±0.003	0.027±0.001	0.315±0.003	0.020±0.001	0.643±0.004	0.213±0.002	Co
Cr	1.40±0.02	0.78±0.01	0.57±0.01	0.09±0.01	0.028±0.005	0.009±0.006	0.038±0.006	0.011±0.005	Cr
Cs	0.014±0.002	0.016±0.001	-	0.081±0.001	0.042±0.001	0.005±0.001	0.045±0.001	0.066±0.001	Cs
Cu	0.15±0.08	<2.3	<0.09	0.35±0.08	0.11±0.08	0.19±0.08	0.19±0.11	<0.09	Cu
Eu	<0.0004	<0.0002	<0.0002	<0.0002	<0.0001	<0.0002	<0.0001	<0.0002	Eu
Fe	23.5 ±0.9	5.66±0.43	15.3 ±1.4	2.73±0.16	2.02±0.14	2.02±0.12	1.98±0.25	1.21±0.14	Fe
Ga	0.05±0.04	-	0.06±0.04	0.06±0.04	0.05±0.04	0.07±0.04	<0.06	<0.06	Ga
Ge	<0.06	-	<0.06	0.05±0.04	0.10±0.04	0.15±0.04	<0.06	0.06±0.04	Ge
H	-	-	-	-	-	-	-	-	H
Hf	-	0.0022±0.0004	-	0.0048±0.0007	0.0013±0.0003	-	0.0065±0.0004	0.0014±0.0003	Hf
Hg	0.029±0.006	-	0.049±0.012	0.080±0.005	0.196±0.005	0.320±0.025	0.160±0.014	0.095±0.009	Hg
I	-	-	0.15±0.02	0.15±0.03	-	0.41±0.03	-	-	I
K	19±3	-	<4	163±8	<4	60±3	54±5	5±3	K
La	0.12±0.01	0.040±0.004	0.053±0.006	0.008±0.002	<0.017	0.003±0.001	0.015±0.011	0.032±0.002	La
Lu	-	-	-	-	-	-	-	-	Lu
Mg	<22	<8	<9	29±7	<15	24±9	<15	<17	Mg
Mn	0.05±0.02	0.128±0.009	0.049±0.007	<0.02	<0.06	<0.02	<0.06	<0.10	Mn
Mo	0.23±0.04	0.08±0.02	0.10±0.01	2.84±0.05	0.32±0.01	0.29±0.02	1.34±0.03	0.53±0.02	Mo
N, %	1.00±0.23	1.83±0.01	1.45±0.01	1.13±0.03	1.39±0.05	0.82±0.06	1.65±0.08	1.13±0.03	N,%
Na	835±5	635±4	326±2	193±2	1249±9	197±2	1594±16	1360±12	Na
Ni	5.44±0.19	1.77±0.11	10.7 ±0.2	1.01±0.08	2.33±0.11	2.60±0.13	3.14±0.84	1.28±0.08	Ni
Pb	<0.24	-	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	Pb
Rb	0.28±0.06	0.10±0.02	0.15±0.06	1.21±0.06	0.28±0.06	0.34±0.06	0.66±0.09	0.29±0.06	Rb
S, %	0.15	0.12±0.01	0.85±0.02	1.15±0.07	0.16±0.01	0.73±0.02	0.10±0.01	0.14±0.01	S,%
Sb	0.264±0.003	0.105±0.001	0.104±0.001	0.920±0.005	0.150±0.001	0.357±0.002	0.252±0.001	0.148±0.001	Sb
Se	0.40±0.01	0.56±0.01	0.47±0.01	0.44±0.02	0.28±0.01	5.34±0.03	0.41±0.01	1.25±0.06	Se
Sm	-	-	-	-	-	0.0015±0.0008	-	0.0007±0.0005	Sm
Sr	0.44±0.08	-	<0.12	0.37±0.11	<0.12	0.12±0.08	0.33±0.08	0.10±0.08	Sr
Ta	-	-	-	-	-	0.013±0.001	-	-	Ta
Th	<0.18	0.0012±0.0004	<0.18	0.17±0.12	<0.18	<0.18	0.0074±0.0004	0.0008±0.0004	Th
Ti	<0.60	<5.4	<0.60	0.69±0.40	<0.57	<0.60	<0.60	<0.60	Ti
U	0.118±0.002	0.035±0.001	0.036±0.001	0.73±0.01	0.043±0.001	0.285±0.003	0.123±0.002	0.046±0.002	U
V	<0.15	<0.055	<0.057	<0.06	<0.063	<0.038	<0.063	<0.072	V
W	-	-	0.05±0.01	-	-	-	-	-	W
Y	<0.15	-	<0.15	<0.15	0.12±0.10	<0.15	<0.15	<0.15	Y
Yb	-	-	0.0011±0.0006	-	-	-	0.0021±0.0004	-	Yb
Zn	1.09±0.09	-	1.14±0.05	0.92±0.02	0.13±0.04	0.85±0.03	0.16±0.06	0.09±0.04	Zn
Temp. (°C)	540	540	540	540	540	540	540	540	
Atmosphere	N_2	N_2	N_2	N_2	N_2	N_2	N_2/steam	N_2/steam	
Shale	Colorado	Colorado	Utah	Antrim	Colorado	Morocco	Colorado	Colorado	

Table 3. Concentration of major, minor, and trace elements in unfiltered retort waters from the LETC controlled-state retort, runs CS-68 through CS-74 (in ppm except as noted) (continued).

Element	CS-68	CS-69	CS-70	CS-71	CS-72	CS-73	CS-74	Element
Al	-	-	-	-	-	-	-	Al
As	15.3 ±2.1	6.27±0.92	8.22 ±1.29	4.61±0.23	5.75±0.42	2.53±0.36	3.97±0.38	As
Ba	0.48 ±0.11	-	0.57 ±0.07	0.097±0.073	-	-	-	Ba
Br	0.094±0.024	0.065±0.012	0.038±0.010	0.084±0.005	<0.48	0.64±0.32	0.33±0.32	Br
C(org),%	0.37±0.01	0.28±0.01	0.42±0.01	0.56±0.01	0.40	0.63	0.32	C(org),%
C(inorg),%	0.76±0.01	1.48±0.01	0.79±0.01	0.53±0.01	0.97	0.36	1.41	C(inorg),%
Ca	20±7	19±3	24±1	15±1	-	-	-	Ca
Cd	0.0024±0.0029	0.0012±0.0008	0.0011±0.0006	-	-	-	-	Cd
Ce	0.010±0.004	-	0.0092±0.0032	0.0037±0.0021	-	-	-	Ce
Cl	321±5	328±5	308±4	266±3	-	-	-	Cl
Co	0.614±0.006	0.648±0.005	0.469±0.004	0.277±0.002	<8.6	<9.5	<8.9	Co
Cr	0.050±0.007	0.061±0.006	0.055±0.006	0.043±0.004	<5.8	<6.7	<6.5	Cr
Cs	0.035±0.001	0.043±0.001	0.043±0.001	0.0056±0.0006	-	-	-	Cs
Cu	0.15±0.08	<0.09	<0.09	<0.09	<0.96	<0.99	<0.96	Cu
Eu	0.0002±0.0001	<0.0001	<0.0001	<0.0001	-	-	-	Eu
Fe	3.40±0.20	4.51±0.56	4.50±0.22	3.52±0.16	2.37±1.60	1.87±1.74	4.26±1.76	Fe
Ga	0.07±0.04	<0.06	0.05±0.04	0.05±0.04	<0.60	<0.60	<0.47	Ga
Ge	0.13±0.04	<0.06	<0.06	<0.06	<0.57	<0.54	<0.57	Ge
H	-	-	-	-	-	-	-	H
Hf	0.0033±0.0004	0.0016±0.0003	0.0049±0.0003	0.0016±0.0002	-	-	-	Hf
Hg	0.150±0.014	0.103±0.013	0.098±0.007	0.050±0.002	0.042±0.0	0.250±0.025	0.023±0.004	Hg
I	-	-	-	-	-	-	-	I
K	44±3	37±3	36±3	19±3	-	-	-	K
La	-	0.055±0.003	-	-	-	-	-	La
Lu	-	-	-	0.00015±0.00008	-	-	-	Lu
Mg	<19	<22	<27	<10	-	-	-	Mg
Mn	<0.07	<0.05	<0.04	<0.02	-	-	-	Mn
Mo	1.39±0.04	0.74±0.02	0.65±0.02	0.15±0.01	-	-	-	Mo
N,%	1.68±0.07	2.97±0.02	1.49±0.02	1.15±0.02	1.69±0.01	1.26±0.06	2.82±0.03	N,%
Na	1780±10	1475±10	1283±10	270±2	-	-	-	Na
Ni	3.73±0.18	1.80±0.82	2.02±0.09	1.96±0.10	2.00±0.78	4.28±0.86	2.06±0.82	Ni
Pb	<0.24	<0.24	<0.24	<0.21	<1.7	<1.7	<1.7	Pb
Rb	0.61±0.06	0.50±0.06	0.50±0.06	0.17±0.06	0.80±0.60	0.72±0.48	0.60±0.48	Rb
S,%	0.12±0.01	0.05±0.01	0.11±0.01	0.09±0.01	0.07±0.02	0.78±0.01	0.05±0.01	S,%
Sb	0.253±0.002	0.314±0.002	0.158±0.001	0.115±0.001	-	-	-	Sb
Se	0.71±0.04	0.60±0.06	0.57±0.04	0.33±0.04	0.59±0.30	7.74±0.40	1.29±0.32	Se
Sm	0.0017±0.0007	0.0006±0.0005	-	-	-	-	-	Sm
Sr	0.21±0.08	0.21±0.08	0.21±0.08	0.21±0.08	0.91±0.64	<0.93	0.73±0.62	Sr
Ta	0.051±0.045	-	-	0.0066±0.0041	-	-	-	Ta
Th	0.0046±0.0005	0.0016±0.0003	0.0094±0.0004	0.0013±0.0003	<1.5	<1.4	<1.4	Th
Ti	0.62±0.40	0.67±0.40	0.81±0.40	<0.57	<18	<22	<21	Ti
U	0.111±0.003	0.075±0.001	0.082±0.002	0.038±0.001	<2.5	<2.5	<2.5	U
V	0.19±0.07	0.07	<0.25	<0.10	<10	<12	<12	V
W	-	0.22±0.04	-	0.047±0.005	-	-	-	W
Y	<0.15	<0.15	<0.15	<0.15	<1.1	<1.1	<1.1	Y
Yb	-	0.0013±0.0005	0.0021±0.0004	0.0012±0.0004	-	-	-	Yb
Zn	0.15±0.03	0.10±0.03	0.26±0.03	0.14±0.06	<0.72	<0.75	<0.72	Zn
Temp. (°C)	540	540	540	540	540	540	540	
Atmosphere	N₂	N₂/steam/O₂	N₂/steam	N₂/steam	N₂/steam	N₂/steam	N₂/steam/O₂	
Shale	Colorado	Colorado	Colorado	Utah	Colorado	Moroccan	Colorado	

Table 4. Concentration of major, minor, and trace elements in unfiltered retort waters from the LLL simulated in-situ retorts (in ppm except as noted).

Element	S-9	S-10	S-11	S-12	S-13	S-14	S-15	L-1	Element
Al	15.9±0.5	16.4±0.5	12.5±0.5	–	–	–	–	–	Al
As	0.47±0.08	1.68±0.08	2.57±0.13	2.61±0.38	0.357±0.002	0.427±0.003	0.284±0.002	0.86±0.01	As
Ba	–	–	–	–	–	–	–	–	Ba
Br	0.53±0.05	0.08±0.04	0.34±0.04	0.320±0.003	0.092±0.003	0.184±0.004	0.271±0.004	0.16±0.01	Br
C(org),%	0.31±0.10	0.36±0.09	0.21±0.04	–	0.24±0.01	–	0.28±0.01	0.20±0.04	C(org),%
C(inorg),%	0.33±0.08	1.76±0.11	1.20±0.02	–	0.404±0.001	–	0.536±0.004	1.24±0.02	C(inorg),%
Ca	–	6±1	21±4	–	–	–	–	<16	Ca
Cd	<0.002	<0.002	<0.005±0.0005	0.054±0.009	–	0.025±0.007	–	–	Cd
Ce	–	–	–	0.027±0.004	–	–	–	0.007±0.003	Ce
Cl	< 5	<6	11±2	368±3	352±3	353±5	370±8	309±3	Cl
Co	< 0.03	<0.81	<0.03	0.0347±0.0004	0.184±0.001	0.030±0.001	0.031±0.001	0.212±0.002	Co
Cr	< 0.4	<0.27	0.39±0.22	0.049±0.004	0.070±0.003	0.306±0.006	2.92±0.02	0.43±0.01	Cr
Cs	–	–	–	0.0074±0.0005	–	–	–	–	Cs
Cu	3.3±0.3	0.87±0.08	133±6	139±6	< 0.9	< 2.1	2.07±0.69	<1.0	Cu
Eu	–	–	–	0.0002±0.0001	0.00008±0.00006	<0.00008	<0.00008	–	Eu
Fe	1.38±0.06	2.34±0.16	27.2±2.2	16.0±2.0	1.71±0.16	28.1±0.4	3.39±0.20	1.7±0.3	Fe
Ga	–	<0.06	<0.09	0.013±0.007	<0.6	<1.3	<0.6	<0.6	Ga
Ge	–	<0.06	<0.06	<0.6	<0.5	<1.2	<0.6	<0.6	Ge
H	–	–	–	–	–	–	–	–	H
Hf	–	<0.12	–	–	–	–	–	0.0020±.0003	Hf
Hg	0.079±0.005	<0.00050	0.085±0.011	0.017±0.002	<0.016	0.044±0.004	<0.017	0.019±0.004	Hg
I	–	–	–	0.25±0.02	0.15±0.01	0.13±0.01	0.16±0.01	0.13±0.02	I
K	–	6±3	26±3	6.6±1.1	5.8±1.1	–	–	18±7	K
La	–	–	–	0.0080±0.0005	0.00094±0.00016	0.00027±0.00013	0.00025±0.00014	0.014±0.016	La
Lu	–	–	–	–	–	–	–	–	Lu
Mg	<40	–	<39	4.3±3.1	4.1±3.0	<9.2	<3.1	<7.0	Mg
Mn	0.22±0.03	0.39±0.03	0.19±0.03	0.175±0.003	0.0022±0.0029	1.01±0.01	0.091±0.003	0.172±0.006	Mn
Mo	–	–	–	–	–	–	0.010±0.005	0.13±0.02	Mo
N,%	–	–	–	–	–	–	–	–	N,%
Na	48±4	45±4	52±3	18.6±0.3	26.0±0.3	3.06±0.11	2.31±0.09	179±1	Na
Ni	0.24±0.03	0.48±0.08	1.57±0.10	1.05±0.07	0.27±0.05	< 2.5	1.01±0.08	<0.31	Ni
Pb	0.06±0.01	<0.24	1.15±0.16	<1.7	<1.7	<3.6	<1.7	<1.7	Pb
Rb	–	<0.09	0.07±0.06	0.032±0.008	<0.7	<1.6	0.019±0.008	<0.018	Rb
S,%	–	–	–	–	–	–	–	–	S,%
Sb	–	–	<0.07	1.102±0.001	0.0033±0.0001	0.0049±0.0001	0.0041±0.0001	0.081±0.001	Sb
Se	0.30±0.02	0.77±0.04	1.09±0.06	1.42±0.01	0.487±0.004	0.465±0.007	0.581±0.004	0.228±0.005	Se
Sm	–	–	–	–	0.00006±0.00004	–	–	–	Sm
Sr	–	<0.12	<0.12	<1.0	<1.0	<2.0	<1.0	<0.27	Sr
Ta	–	–	–	–	0.0056±0.0011	–	–	–	Ta
Th	<0.01	<0.18	<0.01	<1.5	<1.4	<3.0	–	<1.5	Th
Ti	2.4±0.9	<0.57	0.86±0.42	2.7±1.9	2.2±1.6	<2.4	<1.9	<3.5	Ti
U	–	<0.30	<0.30	0.0116±0.0003	0.0155±0.0002	0.0052±0.00002	0.0011±0.0001	0.195±0.002	U
V	0.09±0.01	0.08±0.01	0.08±0.01	0.023±0.017	0.023±0.017	<0.03	<0.03	0.16±0.04	V
W	–	–	–	0.019±0.001	0.011±0.001	0.0057±0.0010	0.0072±0.0009	0.13±0.01	W
Y	–	< 0.15	<0.15	0.8±0.8	<1.1	< 2.3	0.8±0.7	<1.1	Y
Yb	–	–	–	–	0.0014±0.0003	0.00094±0.00070	0.0010±0.0003	–	Yb
Zn	0.10±0.02	0.24±0.06	13.3±0.6	13.2±0.8	<0.7	0.31±0.02	0.62±0.02	0.58±0.03	Zn
Temperature (°C)	494	868	1003	942	887	1010	1025	900–1200	
Atmosphere	N_2	Air/recycle	Air	Air/N_2	Air/steam	Air/steam	Air/steam	Air/N_2	
Shale	Colorado	Colorado	Colorado	Colorado	Colorado	Colorado	Colorado	Colorado	

Table 5. X-ray fluorescence analyses of particulates and filtered retort waters from the controlled-state retort (mg/l).

Element	Filtered	Particulate	Percent Element in Particulates	Filtered	Particulate	Percent Element in Particulates	Filtered	Particulate	Percent Element in Particulates	Element
		CS-60			CS-62			CS-63		
As	6.04 ± 0.30	0.12 ± 0.01	2	6.22 ± 0.31	0.130 ± 0.006	2	1.82 ± 0.09	0.016 ± 0.002	1	As
Br	0.10 ± 0.06	< 0.006	<6	0.15 ± 0.06	<0.007	<4	0.58 ± 0.04	<0.002	<0.3	Br
Ca	13.1 ± 1.0	13.4 ± 0.06	51	5.75 ± 0.98	0.43 ± 0.09	7	5.97 ± 1.2	8.48 ± 0.42	59	Ca
Cr	1.74 ± 0.22	0.15 ± 0.02	8	0.57 ± 0.01[a]	0.43 ± 0.02	43	0.09 ± 0.01[a]	0.058 ± 0.006	39	Cr
Fe	19.2 ± 0.9	4.32 ± 0.21	18	6.60 ± 0.33	8.73 ± 1.35	57	1.30 ± 0.14	1.43 ± 0.07	52	Fe
Ga	0.05 ± 0.04	< 0.006	<11	0.06 ± 0.04	<0.006	<9	0.06 ± 0.04	<0.003	<5	Ga
Hg	<0.001	0.029 ± 0.008	~100	<0.001	0.051 ± 0.009	~100	0.025 ± 0.006	0.055 ± 0.003	69	Hg
K	18.8 ± 2.8	< 0.24	<1	<4.11	<0.23	–	163 ± 8	0.76 ± 0.06	0.5	K
Mn	0.23 ± 0.16	0.03 ± 0.01	14	<0.21	0.065 ± 0.018	–	0.31 ± 0.14	0.022 ± 0.005	7	Mn
Ni	2.06 ± 0.10	3.38 ± 0.16	62	1.34 ± 0.08	9.32 ± 0.14	87	0.98 ± 0.08	0.031 ± 0.003	3	Ni
Pb	<0.24	0.02 ± 0.01	–	<0.24	0.025 ± 0.015	–	<0.24	0.022 ± 0.004	–	Pb
Rb	0.28 ± 0.06	< 0.009	<3	0.15 ± 0.06	<0.009	<6	1.21 ± 0.06	0.004 ± 0.002	0.3	Rb
Se	0.37 ± 0.04	0.032 ± 0.004	8	0.47 ± 0.04	0.043 ± 0.004	8	0.51 ± 0.04	0.004 ± 0.001	1	Se
Sr	0.41 ± 0.08	0.025 ± 0.008	<6	<0.12	<0.012	–	0.20 ± 0.08	0.168 ± 0.008	46	Sr
Ti	<0.60	< 0.053	–	<0.60	<0.056	–	0.69 ± 0.40	0.030 ± 0.011	4	Ti
V	<0.42	< 0.037	–	<0.42	<0.040	–	0.49 ± 0.28	<0.040	–	V
Y	<0.15	< 0.014	–	<0.15	<0.014	–	<0.15	0.003 ± 0.003	–	Y
Solids		2190 ± 160			2984 ± 123			341 ± 41		Solids

Element	Filtered	Particulate	Percent Element in Particulates	Filtered	Particulate	Percent Element in Particulates	Filtered	Particulate	Percent Element in Particulates	Element
		CS-64			CS-65			CS-66		
As	3.66 ± 0.18	0.023 ± 0.001	1	2.47 ± 0.12	0.016 ± 0.001	1	14.1 ± 2.3	0.055 ± 0.003	0.4	As
Br	0.53 ± 0.06	<0.002	<0.4	0.61 ± 0.06	<0.002	<0.3	0.07 ± 0.06	<0.002	<3	Br
Ca	4.13 ± 0.92	<0.03	<1	6.2 ± 1.1	3.19 ± 0.15	34	22.9 ± 1.3	0.57 ± 0.04	2	Ca
Cr	0.028 ± 0.005[a]	< 0.007	<20	0.24 ± 0.20	0.072 ± 0.007	23	0.038 ± 0.006[a]	<0.009	<19	Cr
Fe	1.91 ± 0.14	0.108 ± 0.005	5	0.42 ± 0.12	1.60 ± 0.07	79	1.59 ± 0.25	0.39 ± 0.02	20	Fe
Ga	0.05 ± 0.04	< 0.002	<4	0.07 ± 0.04	< 0.002	<3	0.05 ± 0.04	<0.002	<4	Ga
Hg	0.181 ± 0.005	0.015 ± 0.002	8	0.253 ± 0.025	0.067 ± 0.004	21	0.127 ± 0.014	0.033 ± 0.003	21	Hg
K	<4.0	< 0.06	–	60.3 ± 3.1	0.33 ± 0.05	1	53.6 ± 5.1	0.23 ± 0.05	0.4	K
Mn	0.20 ± 0.14	< 0.005	<2	0.22 ± 0.14	0.014 ± 0.005	6	0.27 ± 0.14	<0.007	<3	Mn
Ni	2.29 ± 0.11	0.036 ± 0.002	2	2.51 ± 0.13	0.094 ± 0.005	4	2.74 ± 1.15	0.29 ± 0.01	10	Ni
Pb	<0.24	0.006 ± 0.004	–	0.19 ± 0.18	0.006 ± 0.005	3	<0.24	0.007 ± 0.005	–	Pb
Rb	0.28 ± 0.06	< 0.002	<0.7	0.34 ± 0.06	0.0047 ± 0.0020	1	0.66 ± 0.09	0.004 ± 0.002	1	Rb
Se	0.35 ± 0.04	0.003 ± 0.001	1	5.79 ± 0.29	0.045 ± 0.002	1	0.49 ± 0.08	0.007 ± 0.001	1	Se
Sr	<0.12	< 0.003	–	0.12 ± 0.08	0.032 ± 0.003	21	0.33 ± 0.08	0.007 ± 0.003	2	Sr
Ti	<0.57	< 0.01	–	<0.60	0.068 ± 0.013	–	<0.60	0.017 ± 0.012	–	Ti
V	<0.39	0.008 ± 0.006	–	<0.42	0.020 ± 0.009	–	<0.42	0.022 ± 0.009	–	V
Y	0.12 ± 0.10	< 0.004	<3	<0.15	< 0.005	–	<0.15	<0.005	–	Y
Solids		248 ± 33			< 1503			337 ± 17		Solids

[a] Neutron activation analysis.

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Table 5.(Cont'd.)--X-ray fluorescence analyses of particulates and filtered retort waters from the controlled-state retort (mg/l).

Element	Filtered	Particulate	Percent Element in Particulates	Filtered	Particulate	Percent Element in Particulates	Filtered	Particulate	Percent Element in Particulates	Element
		CS-67			CS-68			CS-69		
As	3.50 ± 0.18	0.0105 ± 0.0008	0.3	16.9 ± 0.8	0.054 ± 0.003	0.3	7.32 ± 0.93	0.033 ± 0.002	0.5	As
Br	0.38 ± 0.04	<0.001	<0.3	0.16 ± 0.06	<0.002	1	<0.09	<0.002	-	Br
Ca	5.76 ± 0.94	0.075 ± 0.017	1	20.0 ± 6.6	0.16 ± 0.02	1	18.8 ± 2.7	0.28 ± 0.03	1	Ca
Cr	0.011 ± 0.005[a]	0.005 ± 0.003	31	0.050 ± 0.007[a]	0.004 ± 0.003	7	0.061 ± 0.006[a]	0.011 ± 0.005	15	Cr
Fe	1.07 ± 0.14	0.140 ± 0.006	12	3.22 ± 0.20	0.178 ± 0.008	5	4.35 ± 0.56	0.157 ± 0.007	3	Fe
Ga	<0.06	<0.001	-	0.07 ± 0.04	<0.001	<1	0.06 ± 0.04	<0.002	<3	Ga
Hg	0.090 ± 0.009	0.0099 ± 0.0016	5	0.134 ± 0.014	0.021 ± 0.002	11	0.024 ± 0.013	0.079 ± 0.004	77	Hg
K	4.46 ± 2.66	0.038 ± 0.029	1	43.4 ± 3.0	0.20 ± 0.03	0.5	36.7 ± 1.0	0.078 ± 0.042	0.2	K
Mn	<0.21	<0.004	<0.10	0.22 ± 0.14	<0.004	<2	<0.21	0.013 ± 0.004	-	Mn
Ni	1.26 ± 0.08	0.023 ± 0.002	2	3.61 ± 0.18	0.122 ± 0.006	3	1.52 ± 0.37	0.54 ± 0.03	26	Ni
Pb	<0.24	0.0028 ± 0.0026	-	<0.24	0.007 ± 0.003	-	<0.24	0.0075 ± 0.0042	-	Pb
Rb	0.29 ± 0.06	<0.002	1	0.60 ± 0.06	0.0020 ± 0.0012	0.3	0.50 ± 0.06	0.0020 ± 0.0016	0.4	Rb
Se	1.25 ± 0.06	0.0090 ± 0.0008	1	0.71 ± 0.04	0.0034 ± 0.0006	0.5	0.60 ± 0.06	0.074 ± 0.004	12	Se
Sr	0.10 ± 0.08	<0.002	<2	0.21 ± 0.08	0.0017 ± 0.0014	<1	0.21 ± 0.08	0.0035 ± 0.0022	2	Sr
Ti	0.46 ± 0.38	<0.010	2	0.62 ± 0.40	0.008 ± 0.007	1	0.67 ± 0.40	0.013 ± 0.010	2	Ti
V	<0.42	<0.0001	-	0.19 ± 0.07	0.017 ± 0.005	8	0.35 ± 0.28	0.018 ± 0.007	5	V
Y	<0.15	0.0023 ± 0.0018	-	<0.15	<0.003	-	<0.15	<0.004	-	Y
Solids		241 ± 30			219 ± 78			375 ± 1		Solids

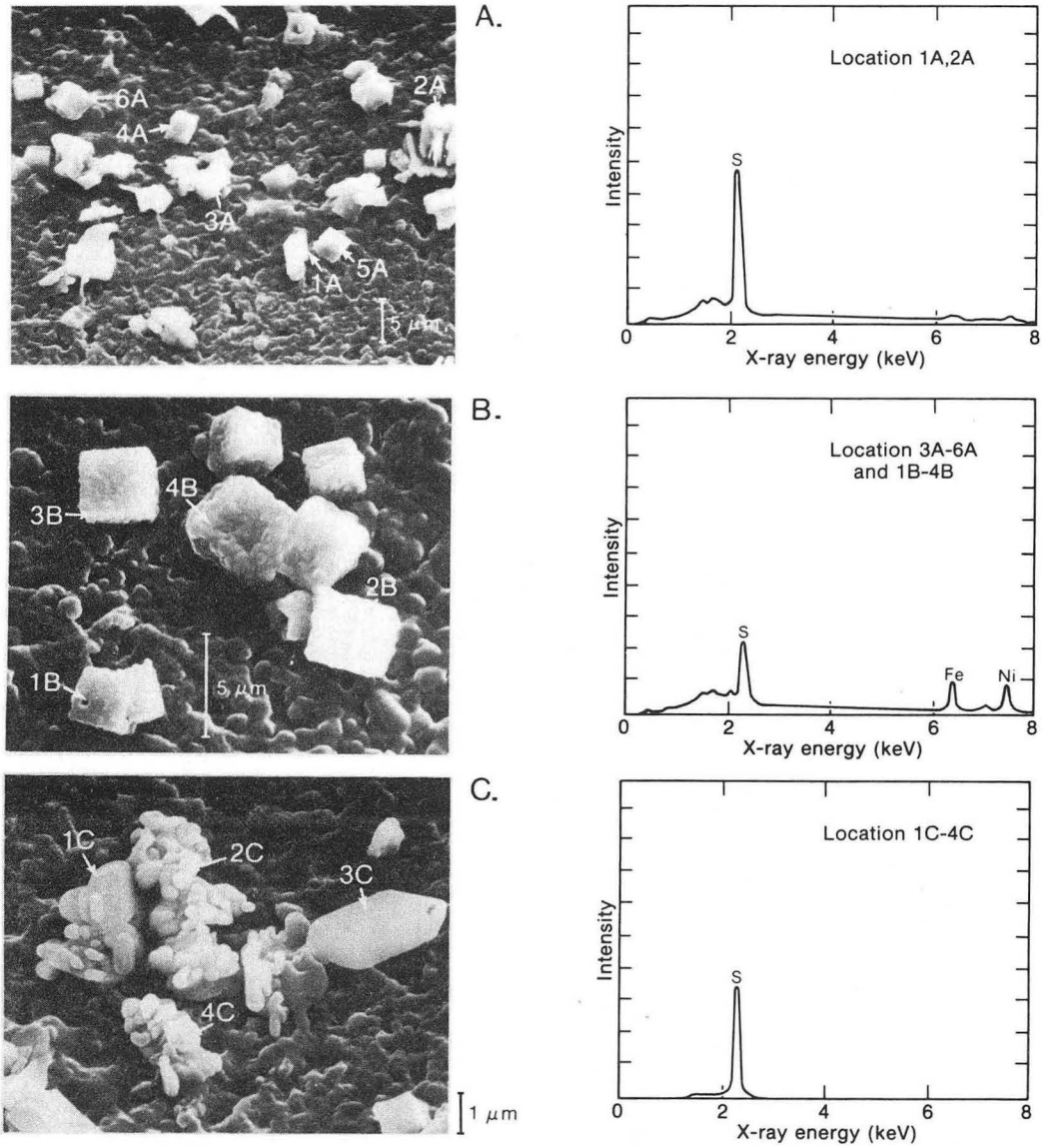| Element	Filtered	Particulate	Percent Element in Particulates	Filtered	Particulate	Percent Element in Particulates
		CS-70			CS-71	
As	7.48 ± 0.37	0.059 ± 0.023	1	4.57 ± 0.23	0.025 ± 0.003	1
Br	<0.09	<0.004	-	0.14 ± 0.04	<0.002	<1
Ca	23.8 ± 1.2	0.34 ± 0.05	1	14.0 ± 1.0	0.93 ± 0.10	6
Cr	0.055 ± 0.006	0.015 ± 0.009	21	0.043 ± 0.004[a]	<0.007	<14
Fe	4.36 ± 0.22	0.135 ± 0.008	3	3.29 ± 0.16	0.23 ± 0.01	7
Ga	0.05 ± 0.04	<0.003	<6	0.05 ± 0.04	<0.002	<4
Hg	0.025 ± 0.007	0.073 ± 0.005	74	0.048 ± 0.002	0.0019 ± 0.0003	4
K	36.1 ± 2.9	0.24 ± 0.09	1	18.7 ± 2.7	0.077 ± 0.043	0.4
Mn	<0.21	<0.010	<0.04	<0.21	0.0076 ± 0.0036	-
Ni	1.52 ± 0.08	0.50 ± 0.03	25	1.94 ± 0.10	0.021 ± 0.003	1
Pb	<0.24	0.011 ± 0.008	-	<0.21	<0.006	-
Rb	0.50 ± 0.06	0.0069 ± 0.0031	1	0.17 ± 0.06	<0.002	<1
Se	0.57 ± 0.04	0.101 ± 0.006	15	0.33 ± 0.04	0.0017 ± 0.0010	1
Sr	0.21 ± 0.08	0.0077 ± 0.0040	4	0.21 ± 0.08	0.0083 ± 0.0022	4
Ti	0.81 ± 0.40	<0.03	<4	<0.57	<0.014	-
V	0.40 ± 0.28	0.018 ± 0.013	5	0.032 ± 0.026	0.008 ± 0.007	2
Y	<0.15	0.0068 ± 0.0048	-	<0.15	<0.004	-
Solids		451 ± 32			203 ± 46	Solids

[a]Neutron activation analysis.

Figure 1. Scanning electron micrograph of (A) particulates from water CS-62;
(B) particulates similar to those at locations 4A-6A in (A); (C) particulates
from water CS-62; and diagrams of x-ray energy at locations 1A; 2A; 3A-6A and
1B-4B; and 1C-4C.
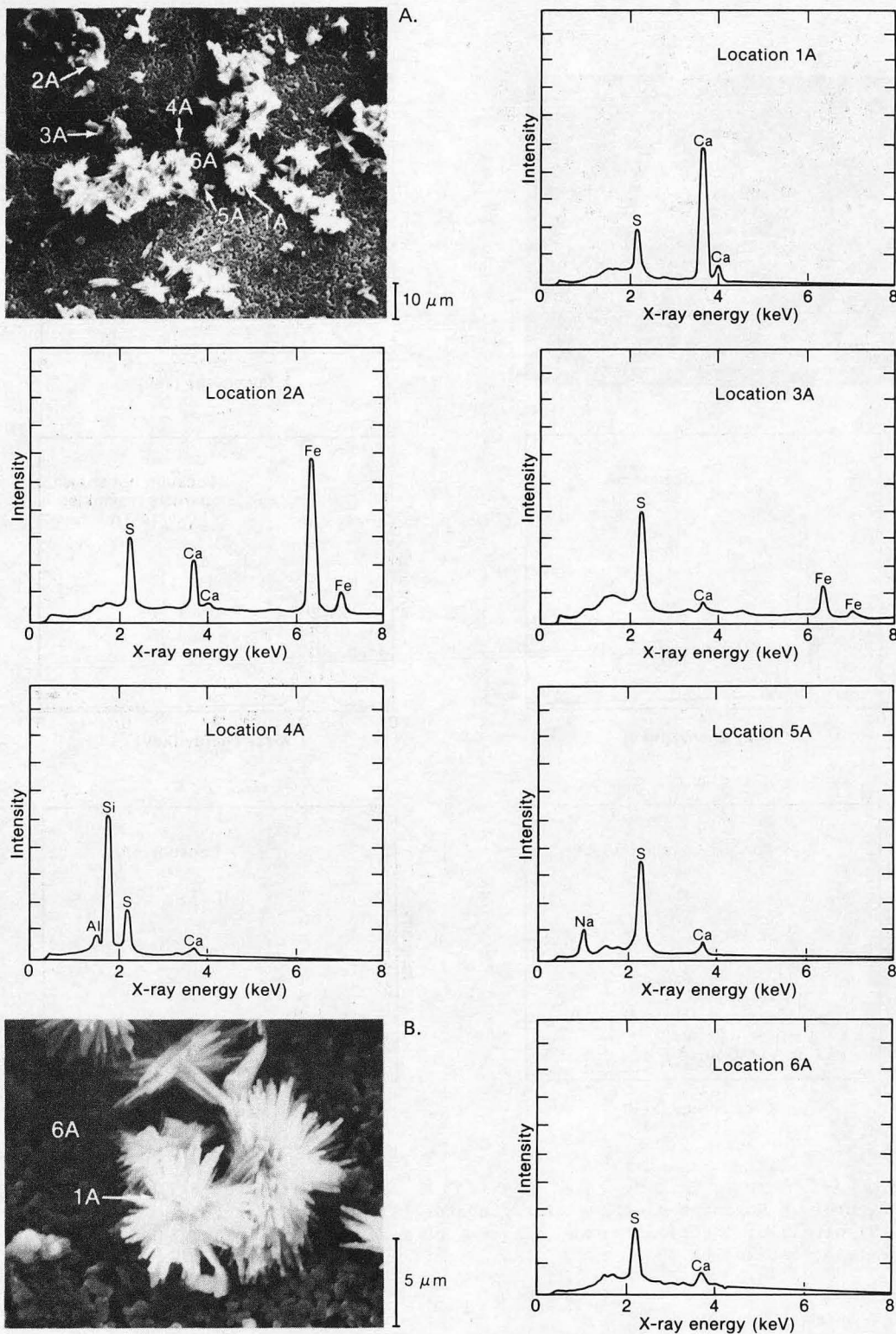
XBB 788-10557A, 58A, and 59A

Figure 2. Scanning electron micrograph of (A) particulates from water CS-64; and diagrams of x-ray energy at locations 1A-4A; 5A; location resembling 1A-7A; and 8A.
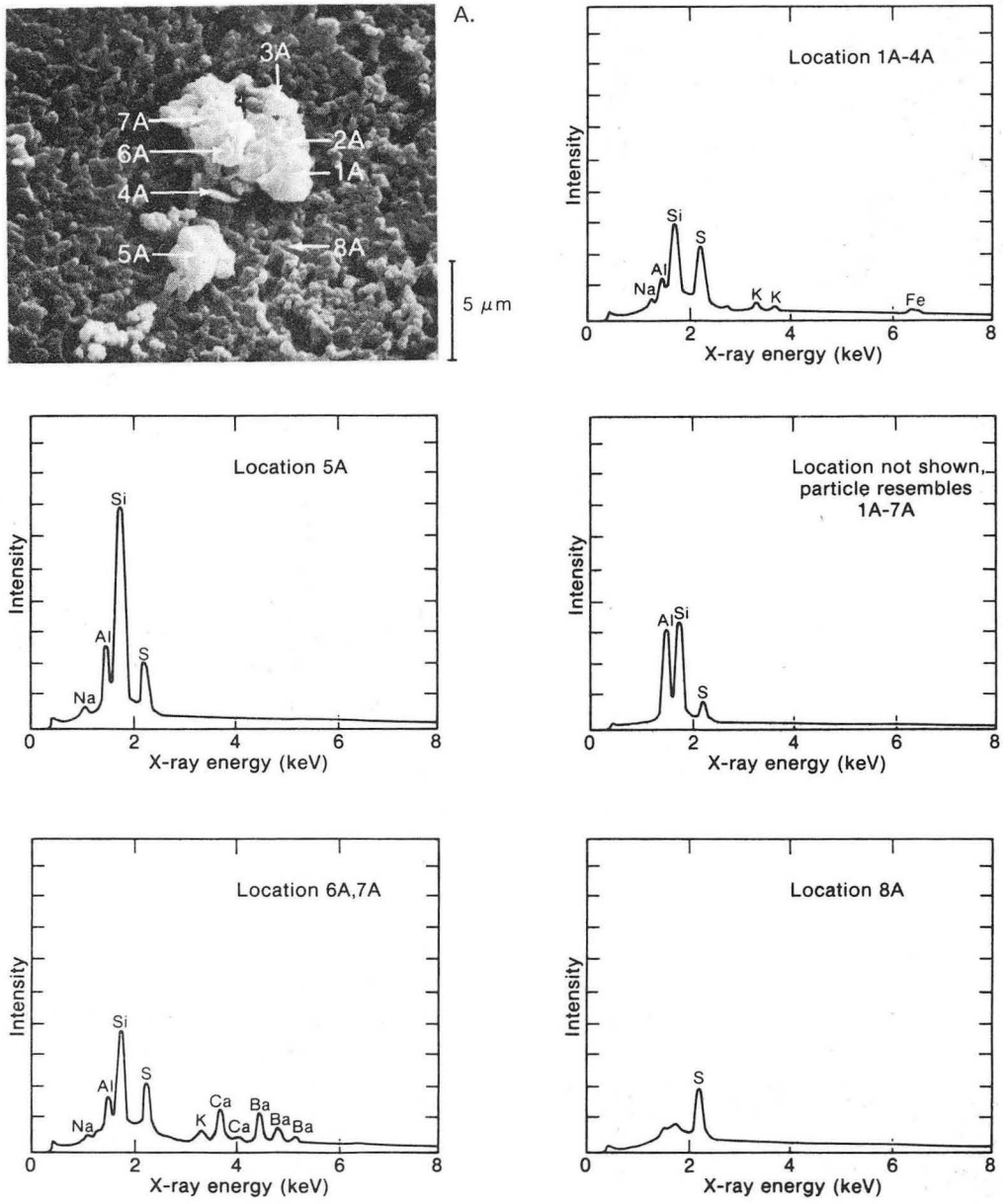
XBB 788-10567A and 69B

Figure 3. Scanning electron micrograph of (A) particulates from water CS-63; (B) detail of location 1A; and diagrams of x-ray energy at locations 1A; 2A; 3A; 4A; 5A; and 6A.

XBB 788-10568A and 68B

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