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SPENT SHALE AS A CONTROL TECHNOLOGY FOR OIL SHALE RETORT WATER

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SPENT SHALE AS A CONTROL TECHNOLOGY FOR OIL SHALE RETORT WATER

INTRODUCTION

Oil shales contain organic material in a mineral matrix. The organic material is pyrolysized to produce shale oil, gas, a solid referred to as spent shale, and aqueous effluents known as retort water and gas condensate. This conversion may be achieved by using various surface or in-situ processes. In the surface processes, shale is mined and pyrolyzed in aboveground retorts. Examples of surface processes include the Paraho, Lurgi, TOSCO, Union B, and Superior processes.

Shale is retorted in the ground in the in-situ processes. Retorts are formed directly in the rock mass, and permeability is introduced by fracturing in true in-situ processes or by mining out a portion of the shale and blasting the balance into the mined-out void in modified in-situ processes. In-situ processes have not been developed to the same degree as surface processes, although several, such as the Occidental, Geokinetics, and Equity processes, are presently being investigated by industry and government.

Both the in-situ and surface processes generate large volumes of spent shale and process water which pose a significant disposal problem for the oil shale industry. These processes produce 0.10 to 22 gallons of water and about 25 to 100 pounds of spent shale for each gallon of oil, depending on plant location and retorting conditions. For a 500,000 barrel per day plant, which represents about six percent of the 1977 U.S. crude oil production, 200 to 400 million gallons of water and one million tons of spent shale may be generated per day. Surface processing produces more spent shale and less water than in-situ retorting.

Viable disposal options must be found for both the spent shale and process water before a commercial oil shale industry can develop. The retort water and gas condensate, which contain high levels of many organic and inorganic constituents, would be a valuable resource for the arid regions in which oil shale deposits are located if effective and economical treatment methods can be developed.

The purpose of this program, which was initiated in June 1978, is to determine whether spent shale can be effectively used in the treatment of in-situ process waters. In-situ processes produce large volumes of retort water and gas condensate, typically from 0.5 to 10 gallons of water per gallon of oil, and they leave large cavities of spent shale underground. If modified in-situ processing is used, about 20 to 40 percent of the in-place shale is mined and may be retorted in surface retorts.

This program is investigating two potential uses of the spent shale for treatment of retort waters (Figure 1). In the first application, the abandoned in-situ retorts would be directly used as part of a treatment system. Water generated in one retort would be circulated through spent shale in an adjacent retort to reduce contaminants in the water and to cool the in-situ spent shale in preparation for retort abandonment and grouting. In the second application, spent shale produced in surface retorts would be used in packed columns similar to powdered activated carbon columns. The

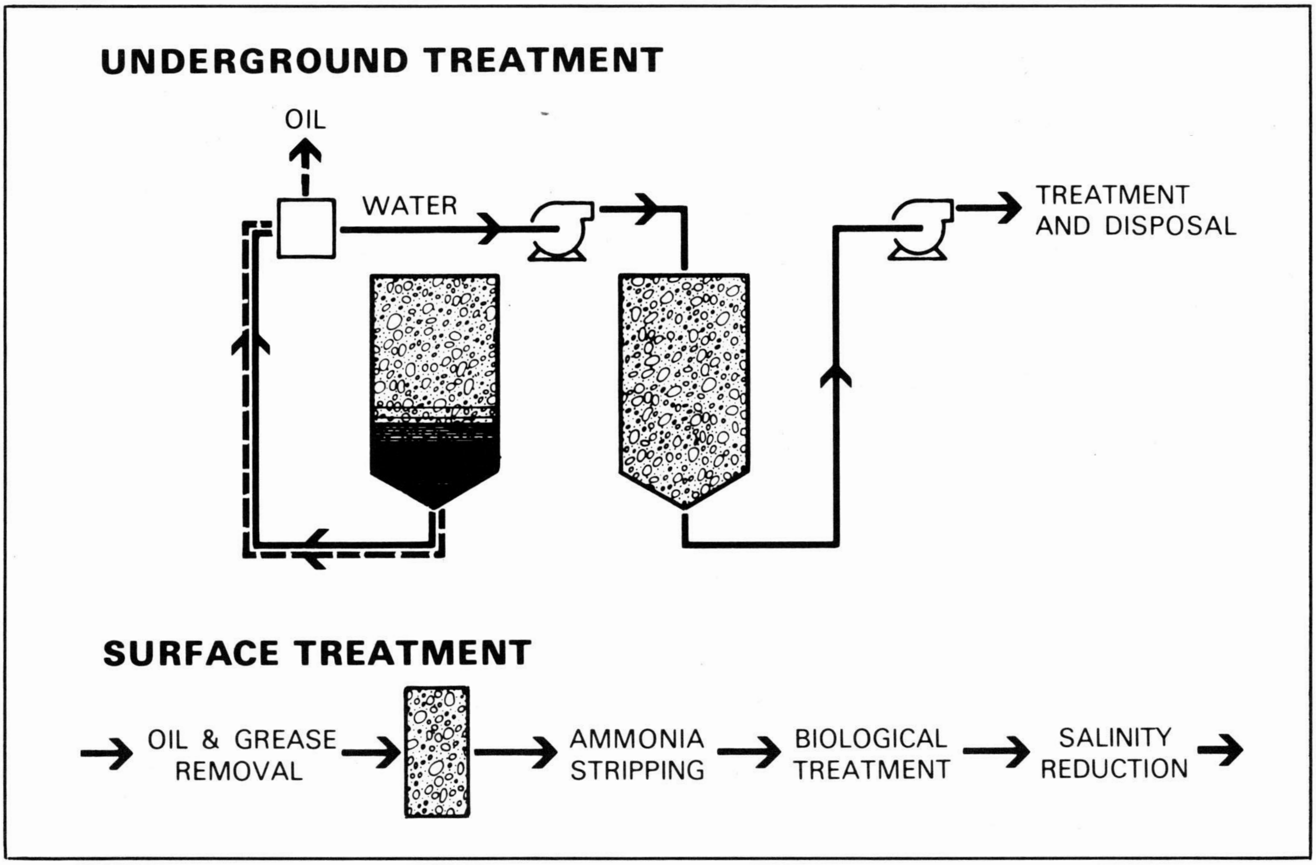

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Figure 1. Potential uses of spent shale in the treatment of retort waters.

exhausted spent shale would be disposed of along with other solid wastes in the on-site solid waste disposal facility.

Past attempts to adapt conventional treatment technologies--such as anaerobic fermentation, activated sludge, carbon adsorption, and chemical oxidation to upgrade these waters--indicate that these methods have serious technical or economic limitations. However, an observation made at Lawrence Berkeley Laboratory during the course of other work suggested that spent shale may be used to upgrade retort waters. A normally non-adsorbing dye, pontacyl pink, was passed through a packed bed of spent shale to facilitate study of the flow of water through the column; the experiment failed because the dye was removed by the column. This observation, supported by subsequent adsorption studies done elsewhere (Hasanain et al., 1977; Stuber and Leenheer, 1978), suggested that spent shale might be used as a treatment step to reduce the level of organic constituents in retort waters. The work summarized here indicates that spent shales are effective in removing color, odor, inorganic carbon, and certain classes of organic compounds, and in elevating the pH of retort water and gas condensates so that NH_3 may be readily stripped.

SUMMARY

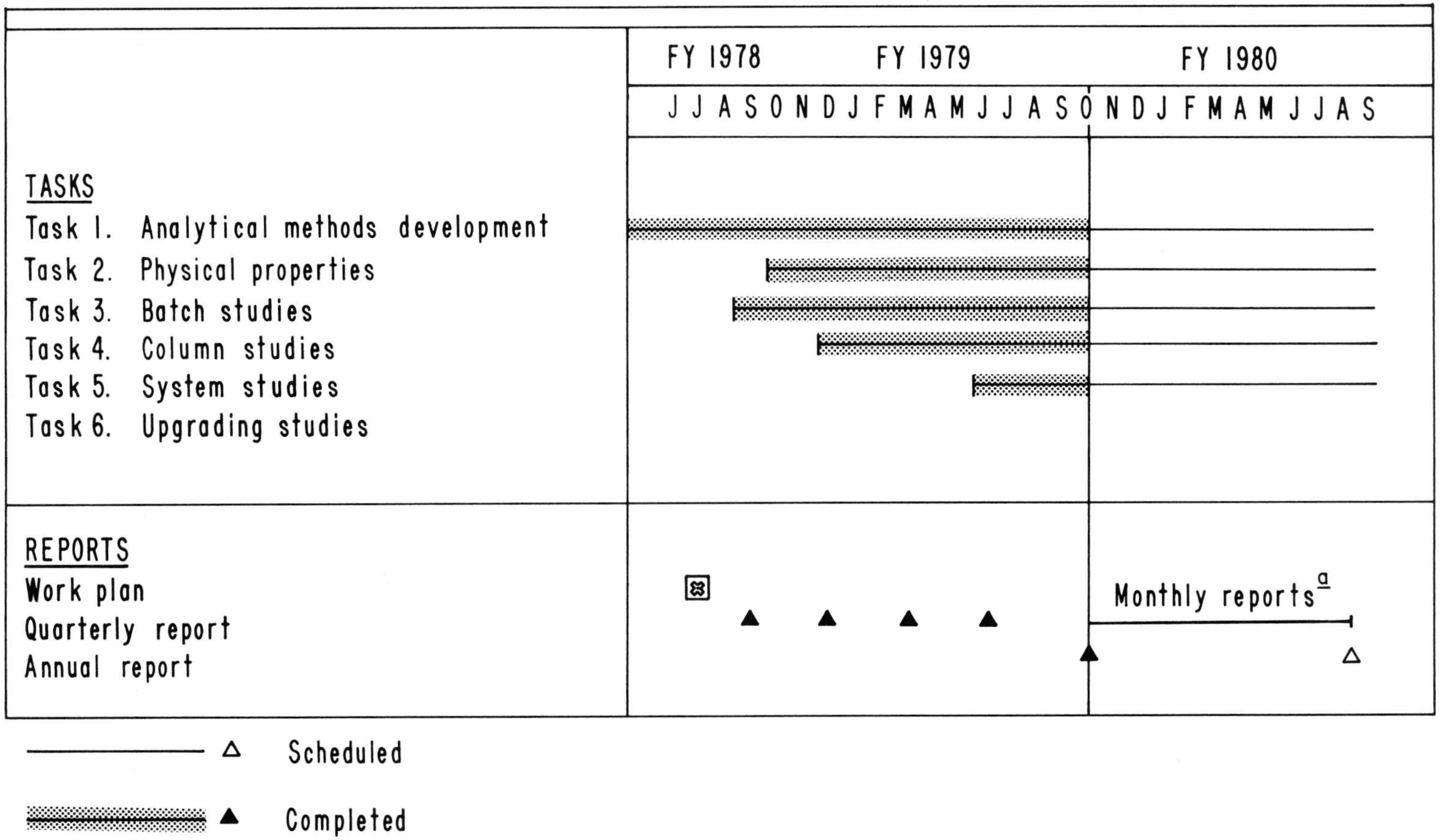
This annual report covers work completed between October 1, 1978, and September 30, 1979. The technical work to be completed on this program is divided into a series of technical tasks which are described in the Work Plan (Fox, 1978) and are shown on the work schedule in Figure 2. Progress of each task during this reporting period is summarized below and described in more detail in subsequent sections of this report. Tasks 1 through 5 are currently in progress.

TASK 1. ANALYTICAL METHODS DEVELOPMENT

An accurate and precise method involving an infrared-combustion (IR) technique was developed to measure dissolved inorganic and organic carbon in retort water and gas condensate. Accurate methods to measure pH and conductivity in these waters were also developed and work was initiated to develop a reliable method of oil and grease analysis. The conventional partition-gravimetric method of oil and grease analysis produced results that were an order of magnitude too high for retort waters due to emulsion formation and extraction of nonmineral hydrocarbons. The new method involves reverse-phase and normal-phase chromatographic separations.

TASK 2. PHYSICAL PROPERTIES

The specific surface area of six spent shales was determined using a Quantsorb BET apparatus. This work revealed that spent shale surface area is almost independent of particle size and is due primarily to internal porosity and residual char. The measured surface areas ranged from 2.1 to 10.2 m^2/g, with the lower values applying to in-situ spent shales and the higher values to surface spent shales.



Notes

[a] Monthly reports will replace quarterly reports starting October 1980

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Figure 2. Work schedule FY 1978, 1979, and 1980.

TASK 3. BATCH STUDIES

Batch studies were conducted using 50 g shale and 50 ml retort water for combinations of six spent shales and four process waters. These studies revealed that spent shales reduce the inorganic carbon, organic carbon, and conductivity and elevate the pH of retort and condensate waters. Organic carbon reduction is proportional to spent shale surface area; and inorganic carbon reduction increases linearly with temperature up to about $700^{\circ}C$ and thereafter levels off at 98 percent. The reduction in inorganic carbon is probably due to reactions between carbonate species in the process waters and hydroxides formed from the hydration of CaO and other metal oxides present in spent shale. An isotherm study suggested that spent shale may not be effective in removing gross organics but may be used for removing specific classes of organic compounds. Acid leaching did not improve the adsorption of organics.

TASK 4. COLUMN STUDIES

A single column study using Paraho spent shale and Geokinetics retort water indicated that spent shales are effective in removing acidic and basic methylene chloride (CH_2Cl_2) extractables. However, since organic carbon breakthrough occurred within two pore volumes, slurry application of spent shale may be more effective than column use.

TASK 5. SYSTEM STUDIES

The batch and column studies indicated that spent shale may be effectively used ahead of an ammonia removal process to reduce inorganic carbon and to elevate the pH to enhance ammonia stripping.

Work was initiated to develop a complete treatment system that includes oil and grease removal, spent shale treatment, ammonia reduction, biological treatment, and salinity reduction. Experiments were conducted to assess coagulation and dissolved air flotation to remove the oil and grease. These studies revealed that the cationic polymers Nalco and Tretolite cause turbidity reductions of 12 to 64 percent for polymer doses of 40 to 160 ppm. These results are not favorable due to the high dosages required.

TECHNICAL PROGRESS

TASK 1. ANALYTICAL METHOD DEVELOPMENT

The purpose of this task is to develop methods for analyzing organic carbon, inorganic carbon, oil and grease, conductivity, pH, and other parameters that will be evaluated in the treatability studies in subsequent tasks; and to use these methods to characterize retort waters.

Reliable chemical characterizations of retort waters are difficult to obtain because of the lack of adequate standards and the limitations of many available analytical methods. Concentrations of many constituents fall outside of the recommended ranges for published methods, and chemical interferences produce inaccurate results. These problems have been identified by many researchers faced with making chemical measurements and have been discussed by Fox et al. (1978). Briefly, retort waters contain high concentrations of many organic sulfur, organic nitrogen, and other compounds that interfere with chemical measurements; precipitates may form on acidification; crystals may form during vacuum filtration; and the waters are highly buffered.

This section will describe the results of work to develop an accurate method for analysis of organic carbon, inorganic carbon, electrical conductivity, pH, and oil and grease.

Process Water Samples

Two types of in-situ oil shale process waters were studied: retort water and gas condensate. Major emphasis was placed on retort waters. Process waters are produced within the retort system as a vapor that is condensed with the oil and gases. These vapors originate primarily from combustion, dehydration of minerals, steam and moisture in the input gas, and groundwater seepage into underground retorts. Most of the oil and water in a commercial plant will be condensed as retort water in an underground product sump at the bottom of the retort. Entrained oil mist and the balance of the water vapor will be removed as gas condensate in a condenser train at the surface. The relative proportions and composition of each type of water depend on the exit gas temperature and the product-collection system design and operation. The retort water travels down the packed bed of shale in an emulsion with the oil, and may leach constituents from the shale matrix and from the oil itself. Because of its contact with the oil and shale, this water can be expected to contain high concentrations of some elements. The gas condensate, on the other hand, leaves 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), mercury, and some organics.

Process waters are produced in large quantities. The volume ratio of water to oil ranges from 0.10 to 22, depending on the type of retort, retorting atmosphere (air or inert gas), and the composition of the oil shale used. Typically, surface retorting processes have a water-to-oil ratio of 0.1 to 0.5 and in-situ processes have a ratio of 0.5 to 1.0.

Retort waters are brown to yellow in color, have a pH that ranges from 8 to 9, contain high levels of many inorganic and organic constituents, and are known to support bacterial growth when maintained at temperatures above 40^{o}F. These waters have high concentrations of solids, NH_3, NH_4, HCO_3, CO_3, and SO_4. The organic constituents are primarily polar, and the principal components are fatty acids and organonitrogen compounds such as pyridines, pyrroles, lutidines, anilines, amines, indoles, and quinolines.

Because the purpose of this program is to investigate the use of spent shale for the treatment of in-situ retort waters, seven separate samples of in-situ process waters were selected for use in these studies. Pertinent retort operating conditions for each of these waters are summarized in Table 1. Most of these waters are from laboratory retorts operated to simulate in-situ conditions because very few in-situ field experiments had been conducted when this work was undertaken. The simulated in-situ retorts from which waters were collected are: the Lawrence Livermore Laboratory (LLL) 125-kg retort (S-13 and S-15), the LLL 6000-kg retort (L-2 and L-3), and the Laramie Energy Technology Center (LETC) 150-ton retort. Three of the samples (Omega-9, Geokinetics, and Occidental) were obtained from actual field experiments. The Omega-9 sample was collected by Farrier et al. (1977) from the 1976 Rock Springs Site 9 true in-situ oil shale combustion experiment conducted by LETC (Long et al., 1977), and has been the subject of an intensive characterization program (Fox et al., 1978). The Geokinetics sample was from a horizontal true in-situ

Table 1. Retort operating conditions and shale characteristics for in-situ process waters.

Water	Retort	Shale source	Shale Size (cm)	Atmosphere	Maximum temperature °C	Isothermal advance rate m/day
S-13	LLL 125-kg	Anvil Points, Colorado	1.3-2.5	Air/Steam	887	2.2
S-15	LLL 125-kg	Anvil Points, Colorado	0.001-2.5	Air/Steam	1025	1.5
L-2[a]	LLL 6000-Kg	Anvil Points, Colorado	0.24-5.1	Air/Steam	890	1.8
L-3	LLL 6000-kg	Anvil Points, Colorado	0.001-3.0	Air/Steam	893	1.3
150-ton	LETC 150-ton	Anvil Point, Colorado	fines-183	Air	816	1.2
Omega-9	LETC Site 9[b]	Rock Springs, Wyoming	---	Air	d	--
Occidental[c]	Retort 6	Logan Wash, Colorado	---	Air/Steam	d	--
Geokinetics	Retort 16	Book Cliff, Utah	---	Air	d	--

[a] Retort water and gas condensate were collected from run L-2. Retort water was taken from the oil collection tank between the retort and the condenser train and gas condensate was taken after the 15°C condenser.

[b] See Long et al. (1977) for a process description and Fox et al. (1978) for a description of water sampling and characterization.

[c] Sample collected from Retort 6 by D. S. Farrier, LETC.

[d] Field retorting temperatures are not accurately known due to corrosion and other problems with thermocouples. However, mineral analyses of spent shales from Occidental field retorts suggest temperatures may reach 1000°C locally.

experiment at Book Cliff, Utah. The Occidental retort water sample was collected by D. S. Farrier of LETC during a steam-combustion experiment on Retort 6 at Occidental's Logan Wash property. This sample will be the subject of an interlaboratory characterization study in 1980 and will be used in the system treatment studies in this program. Characterizations of these samples are summarized in Table 2. Samples S-13, S-15, and 150-ton are a composite of gas condensate and retort water; samples L-2, L-3, Omega-9, and Occidental are retort waters; and a sample of L-2 gas condensate is also included.

Carbon Analyses

The purpose of this work was to systematically investigate the applicability of standard analytical techniques for the measurement of dissolved organic and inorganic carbon in oil shale retort waters and to develop a reliable method for use in subsequent experiments. Preliminary study identified a major discrepancy in the organic and inorganic carbon measured by different methods. An intensive investigation, conducted to resolve this problem, revealed that the infrared-combustion (IR) technique yields accurate measurements of organic and inorganic carbon in retort waters if the standard methods are modified. Dissolved organic carbon can be accurately measured by eliminating carbonates, combusting the sample in an oxygen stream at $950^{o}C$, and measuring evolved CO_2 with a non-dispersive IR spectrometer. Samples are filtered through a 0.45 μm Millipore filter, diluted to less than 100 ppm total carbon, acidified to pH 2 with 85 percent phosphoric acid, and sparged with nitrogen for one to two

Table 2. *Characterization of process water samples used in this work.*

Parameter	150-ton retort water[a]	Omega-9 retort water[b]	S-13 retort water[c]	S-15 retort water[c]	Occidental retort water[d]	Geokinetics retort water[f]
Antimony	—	1.9	0.0033	0.0041	—	0.011
Alkalinity, Total (mg/l $CaCO_3$)	38,000	16,200	—	—	6471[e]	17,840
Aluminum	16.6	<0.03-19.1	—	—	—	—
Arsenic	1.4	1.0	0.36	0.28	0.12	2.55
Barium	0.17	0.71	—	—	—	0.54
Biochemical Oxygen Demand, 5-day (BOD_5)	5,325	740	—	—	—	—
Boron	3.4	27	—	—	17	—
Bromine	1.5	2.4	—	—	—	0.18
Calcium	3.3	12	—	—	<0.1	33
Carbon, Inorganic	6400[e]	3450[e]	—	—	1102	—
Carbon, Dissolved Organic (DOC)	3300[e]	915[e]	—	—	1102	1800[e]
Chemical Oxygen Demand (COD)	8800	8100	—	—	7146[e]	3680
Chlorine	57	824	352	370	540	3016
Chromium	0.018	0.02	0.07	2.92	<0.1	0.078
Cobalt	0.31	0.03	0.18	0.03	—	0.56
Copper	15.6	j0.10	<0.9	2.1	—	0.21
Fluorine	26	60	—	—	42	35
Iodine	0.11	0.59	—	—	—	—
Iron	4.7	1.2	1.7	3.4	—	—
Lead	0.3	0.0045-0.02	<1.7	—	—	14.0
Magnesium	24	20	4.1	<3.1	0.8	17
Manganese	0.22	0.09	0.0022	0.091	—	0.94
Nickel	0.014	0.06	0.27	1.0	—	1.62
Nitrogen, Total NH_3 (as NH_3)	10,150	3795	—	—	970[e]	1270
Nitrogen, Kjeldahl (as N)	11,000	3420	—	—	—	—
pH	8.8[e]	8.78[e]	—	—	9.17[e]	—
Phosphorous (as P)	8.5	3.2	—	—	—	8.56
Potassium	37	47	5.8	—	92	121
Selenium	0.24	0.21	0.49	0.58	0.048	0.22
Silicon	25	8	—	—	—	8.4
Sodium	655	4333	26	—	3625[e]	9392
Solids, Total Dissolved	4210	14,210	—	—	11,650[e]	
Sulfate (as SO_4)	1100	1990	—	—	1900	609
Sulfur, Total (as S)	406	2010	—	—	—	—
Vanadium	1.8	0.12	0.023	<0.03	—	0.43
Zinc	6.4	0.31	<0.7	0.62	—	0.095

[a] Ossio et al., 1978
[b] Fox et al., 1978
[c] Fox, 1980
[d] Analyses by D. S. Farrier, LETC, for LETC sample number ES-79-049 collected 04/11/79 .
[e] Measured in this study
[f] Geokinetics, 1979

minutes to remove carbonates. Dissolved inorganic carbon can be accurately measured by subtracting dissolved organic carbon from the total dissolved carbon determined by the IR-combustion technique. Fresh standards are prepared daily. The resulting samples are injected directly into the 950°C total carbon combustion tube of a Beckman 915A Total Carbon Analyzer.

The development of the above described method and experimental work conducted to validate it are described in subsequent discussions.

Standard Analytical Methods. The organic carbon in aqueous samples is conventionally determined by measuring total carbon and inorganic carbon and computing the organic carbon by difference (the indirect method) or by measuring the organic carbon following elimination of the inorganic carbon (direct method).

In the indirect method, the total and inorganic carbon are measured by injecting the sample into heated combustion tubes which convert the carbon in the sample into CO_2. A flowing oxygen stream carries the gaseous reaction products through a non-dispersive infrared analyzer set to measure CO_2 and the output is recorded as a peak height or peak area. The total carbon is measured in a combustion tube maintained at 950°C and packed with cobalt oxide-impregnated asbestos. At this temperature, inorganic and organic carbon decompose to CO_2. Inorganic carbon is measured in a second combustion tube maintained at 150°C and packed with quartz chips treated with phosphoric acid. This temperature is too low to combust most organic substances to CO_2. The acid-treated packing liberates CO_2 and steam from carbonates (Van Hall and Stenger, 1967).

In the direct method, the inorganic carbon is removed and the sample analyzed using the high-temperature combustion tube. Since the inorganic carbon has been removed, only the organic carbon remaining is measured. Inorganic carbon may be removed by precipitation with barium hydroxide [$Ba(OH)_2$], by acidification and boiling, or by purging with an inert gas (Van Hall et al., 1965). The most frequently used method, the one considered in this work, is acidification and purging with an inert gas.

Experimental Methods. A series of experiments was conducted to determine the effect of some experimental variables on the dissolved organic and inorganic carbon measured by the direct and indirect methods. Variables studied include aeration time, type and strength of acid, the effect of sparging and acidification on organic carbon losses during the direct method, and the effect of dilution on both the direct and indirect methods. An independent method of measuring inorganic carbon was developed as a check on the IR-combustion method. Experimental methods used in these studies are described below.

Apparatus. A Beckman 915A Total Carbon Analyzer equipped with a Beckman 965 non-dispersive infrared spectrometer and a peak area integrator was used to measure total and inorganic carbon in filtered samples of retort water. The instrument was operated according to instructions in the manufacturer's literature (Beckman, 1975).

Reagents and Glassware. Reagent-grade chemicals were used throughout. Materials in contact with standards and samples were Pyrex, borosilicate glass, or polyethylene. All materials that contacted the samples or standards were rinsed with de-ionized Berkeley tap water, soaked and rinsed in concentrated HNO_3, rinsed three times with de-ionized water, and air dried in a plastic positive-ventilation hood.

Standard Curve. A 1000 ppm inorganic stock solution was preprared by dissolving 2.202 g of anhydrous sodium carbonate (Na_2CO_3) and 1.748 g of anhydrous sodium bicarbonate ($NaHCO_3$) in carbon dioxide-free water and diluting to 500 ml in a volumetric flask. A 1000-ppm organic stock solution was prepared by dissolving 1.0624 g of potassium biphthalate ($C_8H_5KO_4$) in carbon dioxide-free water and diluting to volume in a 500-ml volumetric flask. A series of standards was prepared containing 1, 3, 5, 10, 20, 40, 60, and 80 ppm of carbon by pipetting 0.05-ml to 8-ml aliquots of the stock solution into appropriate volumetric flasks, diluting to volume with carbon dioxide-free water and mixing.

Duplicate 50-µl aliquots of each standard and the blank water were successively injected into the appropriate combustion tube at about two-minute intervals, or until the integrator returned to zero, and the peak area determined with the integrator. A Hamilton 50-µl syringe was used for injections. A standard curve was determined at the beginning and at the end of each analysis session to detect any change in instrumental response. The instrument was found to be stable during 8 to 12 hours of continuous operation throughout the experiments.

Procedure for Preparing Carbon Dioxide-Free Water. Carbon dioxide-free water was prepared by boiling de-ionized water with several glass chips for 30 minutes in an Erlenmeyer flask loosely covered with aluminum foil. After cooling, the flask was fitted with a one-hole stopper attached to $CaCl_2$, ascarite, and soda lime drying tubes in series.

Sample Preparation. A large volume of each water was vacuum filtered through 0.4-μm silver metal membrane filter paper and stored at 4°C in 2-liter polyethylene or glass containers. A 250-ml aliquot was subsampled and stored separately in a second polyethylene bottle. Aliquots of the 250-ml sample were prepared for analysis by transferring appropriate volumes into volumetric flasks, diluting to volume with carbon dioxide-free water, and mixing. All sampling was done during continuous stirring with a Teflon stir bar on a magnetic stirrer. Eppendorf micropipettes with disposable plastic tips were used to transfer the sample. The 250-ml and the 2-liter samples were periodically analyzed to determine the effect of continuous stirring and of the sample containers on organic carbon. No significant difference in the organic carbon levels in the two containers was found.

For the direct method, a 10-ml aliquot of each dilution was transferred to a 4-dram (14.8 ml) glass vial, acidified, and sparged for a specified time with nitrogen at a flow rate of 150 to 200 ml/min. The sparging system is capable of handling four samples simultaneously and consists of four capillary eye droppers suspended from a glass manifold by Tygon tubing. Following sparging, each vial was covered with aluminum foil, capped, and refrigerated at 4°C until analysis. Holding time never exceeded 24 hours.

For the indirect method, a 10-ml aliquot of each dilution was transferred directly into a 4-dram (14.8 ml) glass vial, covered with aluminum foil, capped, and refrigerated at 4^oC until analysis. Holding time never exceeded 24 hours.

Vacuum Transfer Method for Inorganic Carbon. An accurate measurement for inorganic carbon is required to determine organic carbon by the indirect method. The IR-combustion method of measuring inorganic carbon initially produced unreliable results. The measured inorganic carbon decreased as sample dilution increased. Therefore, an independent method was developed to measure inorganic carbon. In this method, the addition of acid to a sample shifts the H_2CO_3-HCO_3-CO_3 equilibrium such that H_2CO_3 is the predominant component. At low pH, the solubility of H_2CO_3 is low and CO_2 will be evolved from solution. As the CO_2 is removed from solution, the equilibrium is shifted until essentially all the inorganic carbon, originally present as HCO_3 and CO_3, is removed.

Five ml of sample were added to a 25-ml long-neck Pyrex flask. The flask was sealed and the contents immediately frozen by immersing it in a liquid-nitrogen-filled Dewar flask. After about three minutes, 1 ml of concentrated phosphoric acid (H_3PO_4) was added to the now solid sample. The flask was then re-immersed in the Dewar flask and connected to the vacuum transfer system. The whole system (the sample flask with frozen contents and the gas transfer system consisting of four traps, Toepler pump, gas buret, and vacuum system manifold) was then evacuated (Figure 3).

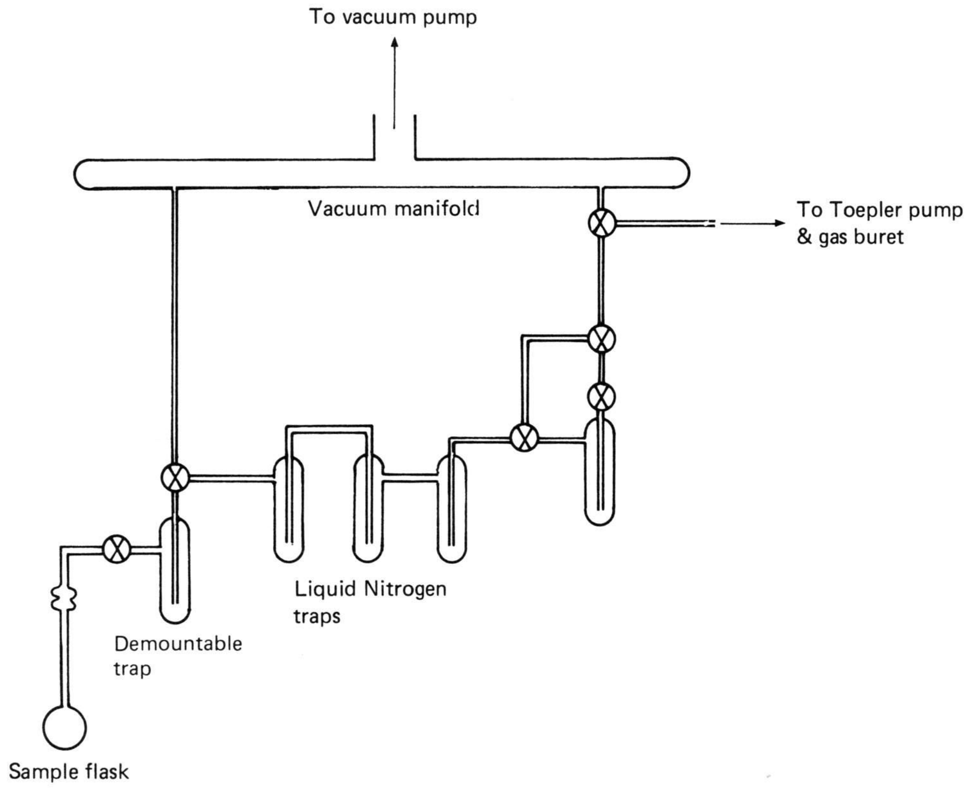

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Figure 3. Experimental setup used to measure inorganic carbon by the vacuum transfer method.

The four traps included a dry-ice/trichlorethylene trap to remove water as well as most organic compounds distilled from the sample flask. This particular trap was demountable and any solution collected was recovered for further analysis. The three liquid-nitrogen traps removed gases such as CO_2 and SO_2, which are condensable at liquid nitrogen temperatures. Volatile organics, except CH_4, that do not condense at dry-ice temperature were also removed.

The sample was then warmed and CO_2 was evolved as the H_3PO_4 mixed with the sample. The sample flask was gently warmed and the degassing continued until outgassing was no longer observed. The heat was removed and pumping continued until the solution began to freeze. The sample flask and first trap were then isolated from the rest of the system. The traps were warmed and the evolved gases transferred with a Toepler pump to a gas buret for measurement of volume and pressure. Finally, the gases were transferred to sample bulbs for analysis by a mass spectrometer. The collected gas was essentially all CO_2. From the number of millimoles of CO_2 collected in each sample, the amount of inorganic carbon expressed as mg carbon per liter of solution was determined. The pH in the degassed water was found to be 2, which is low enough to assure that all of the inorganic carbon originally present as HCO_3 or CO_3 would have been removed as evolved CO_2.

Results and Discussion

Elimination of Inorganic Carbon. In the direct method of analysis, inorganic carbon is removed from solution and the sample directly analyzed on the total channel for organic carbon. Inorganic carbon is usually removed by acidifying the sample to pH 2 or less and removing the CO_2 by purging with nitrogen (Standard Methods, 1976; EPA, 1974; ASTM, 1978). The effect of aeration time and acid strength and type on the removal of inorganic carbon was studied. Two separate samples of retort water were prepared in dilutions of 1:50 and 1:200; acidified to pH 2 with both 2 N and concentrated H_3PO_4 and HCl; and separate 10-ml aliquots were sparged with nitrogen for 1 minute, 5 minutes, and 10 minutes at 150 ml/min. Each aliquot was then analyzed for inorganic carbon. The inorganic carbon in all of the samples was below the detection limit of the method, which indicates that the standard procedure (10 minutes nitrogen purge at pH 2 or less) for eliminating inorganic carbon is suitable for retort waters. Essentially complete elimination of 60 to 110 mg/l of inorganic carbon was obtained at pH 2 with 1 minute of purging at a nitrogen flow rate of 150 ml/min. This is more effective than previously noted by Van Hall and others (1965), who observed that a synthetic sample containing 41 mg/l of inorganic carbon contained 16.9 mg/l of carbon after one minute of purging at 100 ml/min. The type or strength of acid had no effect on the removal of inorganic carbon within the range of variables studied.

A relatively large volume (compared to most water and waste samples) of acid was required to lower the pH of retort waters because they are well buffered by the carbonate and ammonia systems. The recommended 0.1 ml of concentrated HCl may not be adequate (American

Public Health Assoc., 1976) for retort waters and pH measurement should determine the amount of acid required. The volume of 2 N and concentrated acid required to lower the pH of a 30-ml sample of the 150-ton water to pH 2.0 is summarized in Table 3, together with the resulting dilution corrections. This table shows that a significant quantity of 2 N acid is required to adjust the sample pH to 2. This introduces an error in the dilution of from 0.75 to 5.8 percent. The required volume of concentrated acid, on the other hand, results in a dilution correction of from 0.12 percent to 0.25 percent, which is considered negligible. Less concentrated H_3PO_4 than HCl is required to effect the same reduction in pH. For this reason, it is recommended that the sample be acidified to pH 2 with concentrated H_3PO_4. An additional factor in selecting H_3PO_4 over HCl is that the reagent blank obtained for H_3PO_4 was consistently lower than for HCl.

The Effect of Dilution on the Direct and Indirect Method. The effects of dilution on the total, organic, and inorganic carbon content measured by the direct and indirect methods were investigated to identify any analytical problems. Two sets of samples consisting of 1:50, 1:100, 1:250, 1:500, 1:1000, and 1:1600 dilutions were prepared from each of three waters, S-13, S-15, and 150-ton. One set of samples was transferred directly to 4-dr (14.8 ml) glass vials, covered with aluminum foil, and analyzed by the indirect method. The other set of samples was transferred to 4-dr (14.8 ml) glass vials, acidified to pH 2 with concentrated H_3PO_4, sparged with nitrogen for 10 minutes at a flow rate of 150 ml/min, and analyzed directly for

Table 3. Amount of acid required to lower the sample pH to 2.0 for a 30 ml aliquot of 150-ton retort water.

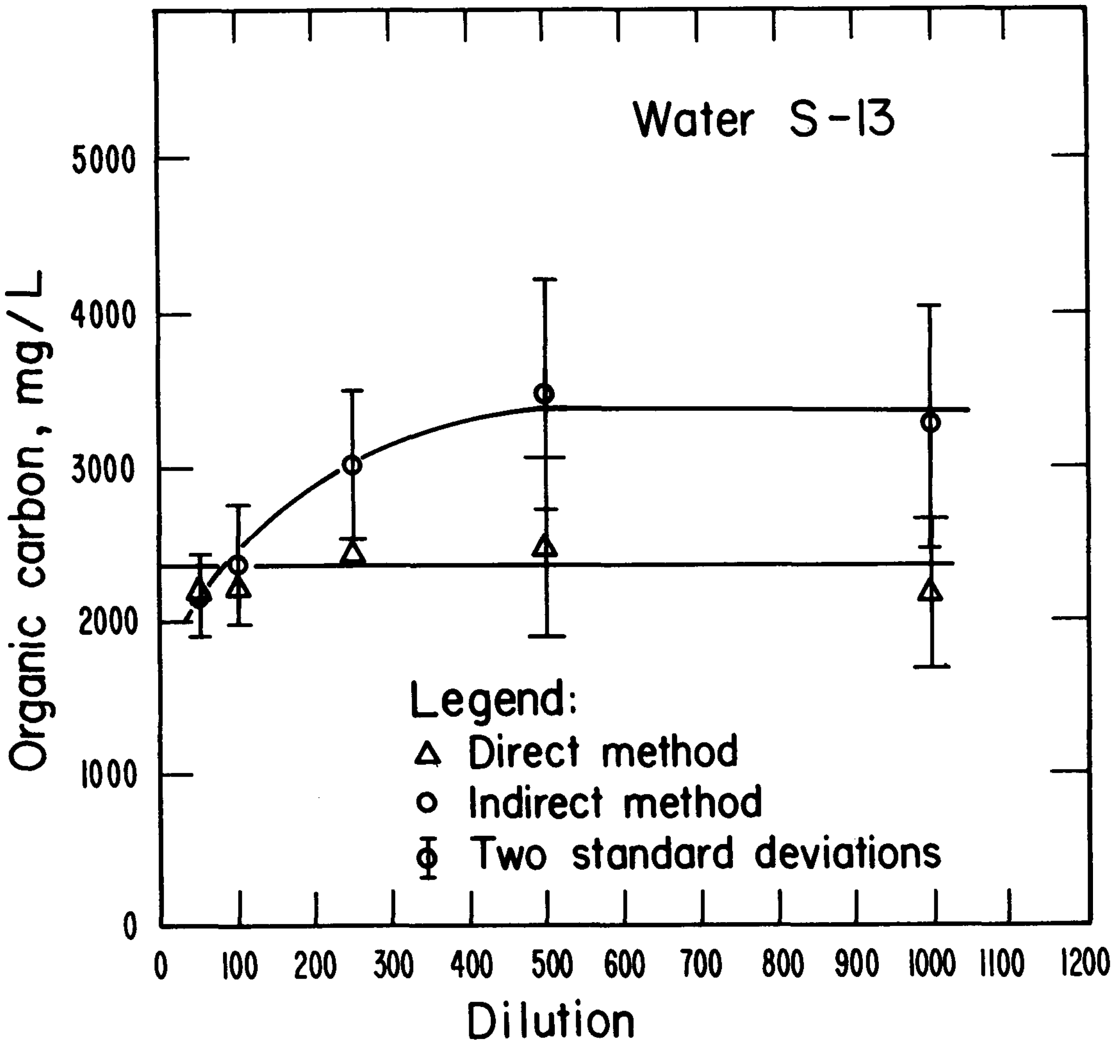
	1:50 dilution		1:200 dilution		1:1000 dilution	
Acid	µl acid to lower pH to 2.0	% error in dilution	µl acid to lower pH to 2.0	%error in dilution	µl acid to lower pH to 2.0	%error in dilution
2 N HCl	375	1.25	225	0.75	-	-
12 N HCl	75	0.25	40	0.13	-	-
2 N H_3PO_4	1750	5.8	1100	3.7	-	-
43.8 N H_3PO_4	55	0.18	35	0.12	35	0.12

organic carbon. The indirect dilution experiment was repeated on four separate days by three analysts, and the direct dilution experiment was repeated on three separate days by three analysts.

Typical results from these experiments are summarized in Figures 4, 5, and 6. These figures indicate that there is no dilution effect for organic carbon measured by the direct method. Within the limits of error of the method, the same value was obtained for the organic carbon by the direct method, irrespective of the dilution. However, a considerable dilution effect was observed for the indirect method of carbon analysis, and the organic carbon measured by the direct and indirect methods did not agree.

Based on these results, additional experiments and analyses were conducted to determine the source of the discrepancy and the dilution effect. This work revealed that the indirect organic carbon problem (dilution effect) was due to the method of preparing and storing the standards used for inorganic carbon. Inorganic standards were prepared monthly and refrigerated in a glass-stoppered flask. It was found that standards prepared and stored in this way are 2 to 4 ppm higher in inorganic carbon after 1 week of storage than freshly prepared standards. This increase in value is due to the uptake of atmospheric CO_2 by the refrigerated alkaline standards.

The small underestimate in the value of the samples created by this error is multiplied by a large dilution factor (100 to 1000) when retort waters are analyzed. The high carbon levels in these waters fall outside of the linear range of the Beckman analyzer and dilutions



XBL 796-1841

Figure 4. The effect of dilution on organic carbon measured by the direct and indirect methods for water S013.

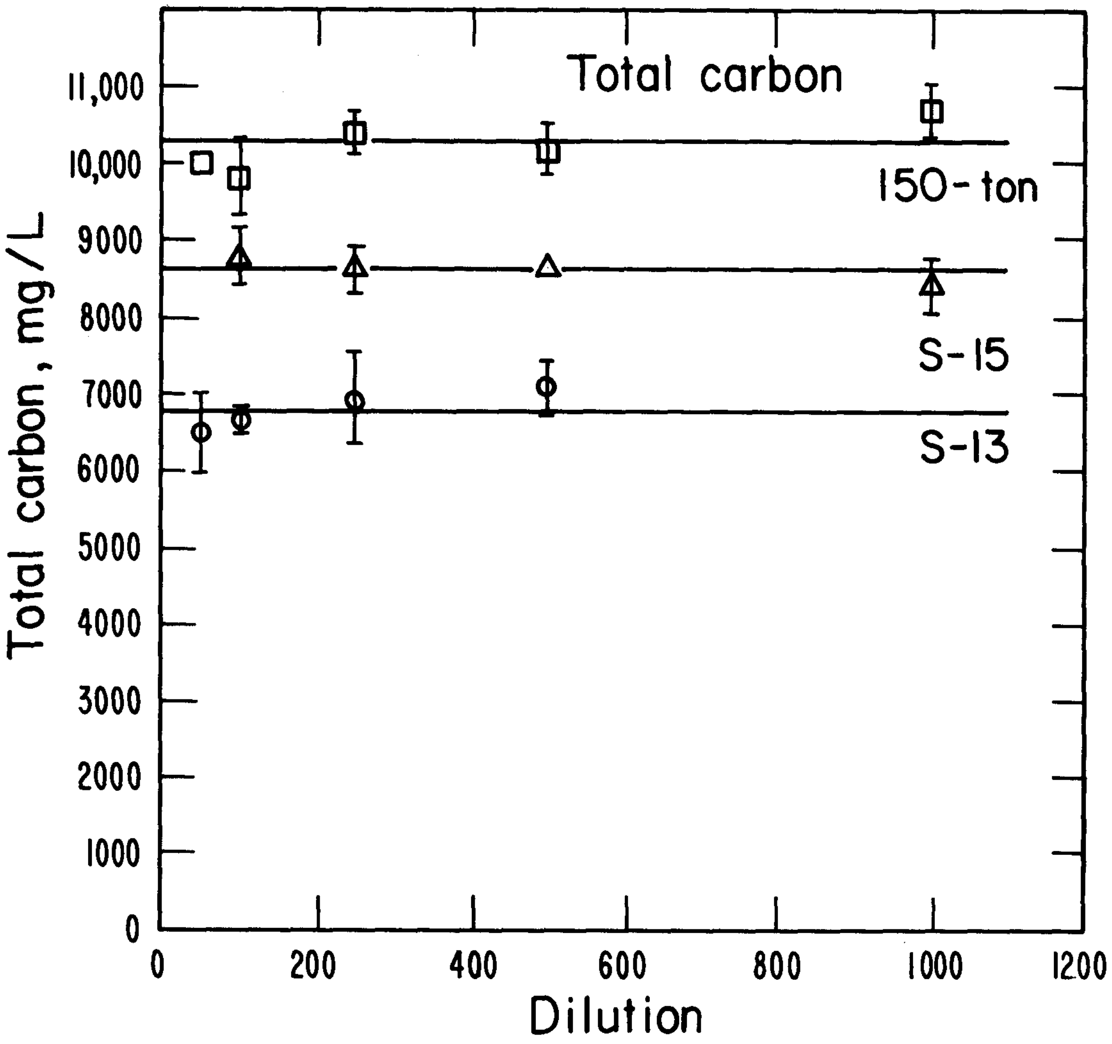


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Figure 5. The effect of dilution on total carbon measured by the IR-combustion method.

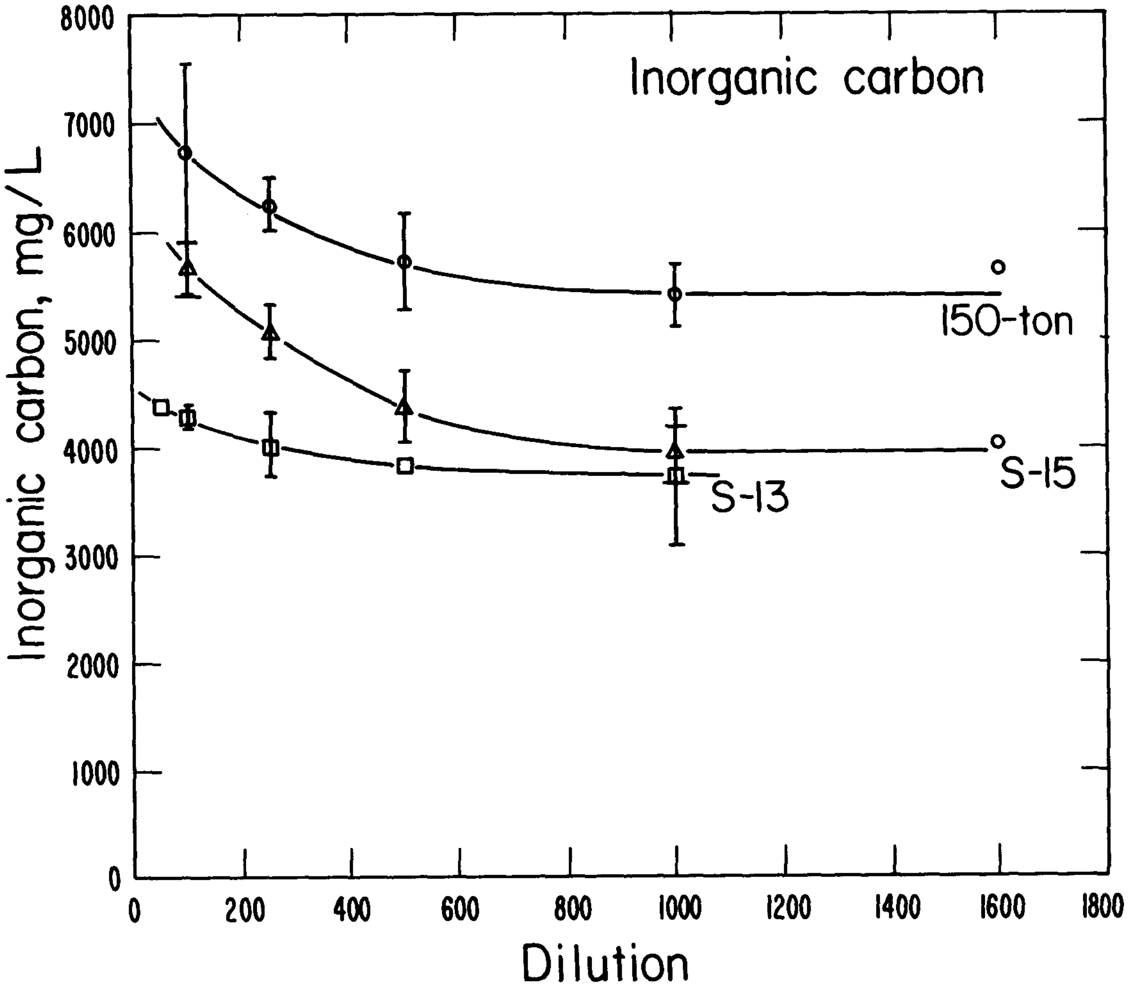

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Figure 6. The effect of dilution on the inorganic carbon measured by the IR-combustion method.

are required. Thus, an error of 3 ppm becomes an error of 3000 ppm, almost 50 percent of the true value. Since the standards are in error by a constant increment (2 to 4 ppm), the deviation between the measured and actual value in diluted samples increases as the dilution does, thus causing the type of curves shown in Figures 3-6. This is not normally a problem for other samples as large dilutions are not required to bring the samples within the working range of the instrument used.

Validation of Direct Method of Organic Carbon Measurement. Fox et al. (1978) indicate that the direct method may produce a low result for organic carbon because volatiles are stripped from solution during purging and acidification results in the precipitation or adsorption of organics. Retort waters are known to contain high concentrations of thiosulfate (S_2O_3) (Fox et al., 1978), which precipitates elemental sulfur on acidification. This precipitate could act as an adsorbent for organics in the water. Retort waters are also known to contain high concentrations of normal carboxylic acids (Cook, 1971; Ho et al., 1976). The higher molecular weight carboxylic acids may precipitate from solution when the pH is lowered. This would directly reduce the organic carbon content and provide a surface for adsorption of other organics. Both of these precipitates would create a sampling problem.

It has also been proposed that the lower molecular weight carboxylic acids, such as acetic acid ($C_2H_4O_2$), may be stripped from solution during purging. However, the results of work by Van Hall et al. (1965) indicate that this is not likely. These investigators demonstrated that these compounds are not volatilized during purging because of their high solubility in water.

The loss of volatiles, precipitation of carboxylic acids, and adsorption of organics were investigated for the three retort waters and found to be insignificant for the samples analyzed. The simplest method of monitoring these types of losses is to make an independent determination of CO_2 and subtract it from the total carbon to determine organic carbon. This was done by degassing acidified retort water in vacuo, collecting the evolved CO_2 in a liquid nitrogen trap, and then transferring it to a gas buret for volume measurement with a Toepler pump (vacuum transfer method), as described previously. The evolved gas was analyzed by mass spectrometry and found to contain only low concentrations of SO_2, presumably from the conversion of S_2O_3 to S and SO_2. No organic constituents were detected, indicating that noncondensable volatile organics (i.e., CH_4) are not stripped out during a N_2 purge.

The results of these independent measurements of organic carbon are summarized in Table 4. This table compares the organic carbon obtained using the direct method (column 4) with the organic carbon obtained by subtracting the independent measurement of inorganic carbon (column 2) from total carbon determined by the IR-combustion method (column 1). The two values reported for the organic carbon (columns 3 and 4) agree to within one standard deviation of the

Table 4. Comparison of dissolved organic carbon determined by direct method with that determined by subtracting inorganic carbon (vacuum method) from total carbon (IR-combustion method). All values are ppm.

Retort Water	Total Carbon (by IR combustion) (1)	Inorganic carbon as evolved CO_2 determined by vacuum method (2)	Organic Carbon (by subtraction) (3)	Organic carbon (by direct method) (4)
150-ton	9870 ± 350	6404 ± 43	3466 ± 353	3300 ± 140
S-13	6260 ± 200	4040 ± 2	2220 ± 206	2300 ± 120
S-15	7850 ± 200	5358 ± 48	2492 ± 208	2600 ± 120

reported error for the 150-ton water and the S-13 water and to within two standard deviations for water S-15. This suggests that no organic carbon is lost during acidification and purging during the direct method, within the limits of the reported errors.

Other independent checks on possible organic loss by volatilization, precipitation, or adsorption were also made. Samples were acidified, sparged with nitrogen, and then returned to pH 8 with solid Na_3PO_4. No significant differences between the organic carbon in these samples and the acidified samples were found, indicating that organic precipitates were not being redissolved. In another experiment, traps shown in Figure 7 were designed to collect organic volatiles during sparging. The sparging stream was passed through an acidified water trap chilled with an ice-H_2O bath. This showed that <100 ppm carbon was retained in the trap. In still another experiment, the 150-ton water was acidified and degassed under vacuum for 5 hours and organics trapped in a dry ice-trichloroethylene (C_2HCl_3) trap. The organic carbon in the trap condensates was 500 mg/l. This value represents an upper limit for the amount of organic carbon that may be lost during the direct method. The experimental conditions (vacuum-induced frothing of undiluted retort water during 5 hours of collection) are much more extreme than those experienced by sparging samples (1 minute sparging at atmospheric pressure).

Source of Error. A number of sources of experimental error were investigated. These include pipetting, volume of acid required for dilution, CO_2 uptake during analysis, and sample stability.

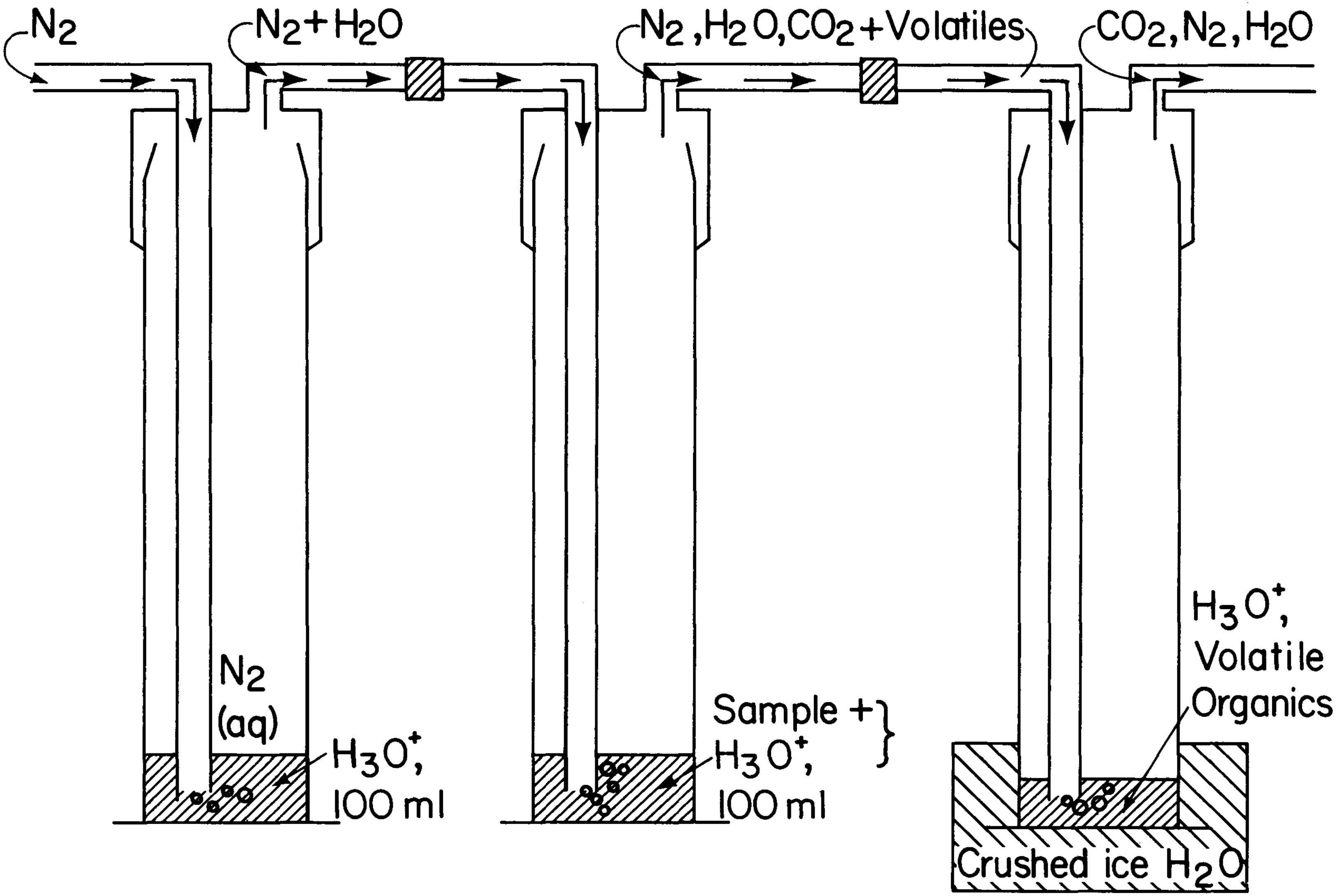

Figure 7. Train for trapping organics during acid sparging of shale waters. XBL 796-1846

It was suspected that the presence of oils, grease, and salts of carboxylic acids in retort water interfered with the pipetting of microliter volumes of water. This was investigated by repetitively pipetting specified volumes of distilled water and retort water into a small container on a microbalance. Two types of micropipettes (Eppendorf and Finn) equipped with disposable plastic tips were investigated. This exercise indicated that retort waters can be accurately pipetted with these micropipettes. However, the pipetting error is about twice as great for retort waters as for distilled water, suggesting that there is a slight transfer problem. The pipetting error for the fixed-volume Eppendorf pipettes was less than 1 percent for volumes of 100 µl to 250 µl, and the error for variable-volume Finn pipettes was about 2 percent for volumes of 100 µl to 250 µl. If these, or similar pipettes, are used for dilutions, it is recommended that they be calibrated for retort water before use and that their reproducibility be tested.

The error associated with acidification in the direct method is less than 0.3 percent if one drop of concentrated H_3PO_4 is used. This is considered to be negligible.

Because of the composition of retort water, the necessity to store it at 4^oC, and the procedures required to get a homogenous sample, ample opportunity exists for exchange of CO_2 between the sample and the atmosphere. This could occur during sampling because the container is continuously stirred while aliquots are withdrawn. It could also occur during sample analysis, particularly if the sample was mixed before withdrawal in a syringe. The magnitude of this effect was investigated by preparing aliquots of three waters at the 1:500 dilution and analyzing them for total and inorganic carbon at 4-hour intervals following both quiescent standing and agitation. No significant uptake of CO_2 was observed, suggesting that uptake does not occur during a normal 8-hour session at the analyzer.

The stability of samples stored at 4^oC was investigated by analyzing aliquots of each of the three samples over a 1-month period. No statistically significant change in organic or inorganic carbon was observed.

Recommended Organic Carbon Method. Based on work completed to date, we recommend the direct method to measure organic carbon in retort waters. The analytical error associated with the direct method is lower than with the indirect method, due to error propagation considerations. Additionally, we encountered problems with the measurement of inorganic carbon by the IR-combustion method required for the indirect method.

In the direct method, the carbon present as bicarbonate or carbonate was removed by acidification and purging with nitrogen. In our work, 10 ml of diluted retort water were brought to pH 2 with concentrated H_3PO_4, and sparged for 10 minutes with nitrogen at a flow rate of 150 ml/min. The inorganic carbon remaining in the samples was found to be lower than the detection limit of the combustion-IR method (<1 ppm). Essentially, complete elimination of as much as 128 ppm of inorganic carbon was obtained in this way. Loss of organics by volatilization, precipitation, or adsorption was demonstrated not to be a problem for the three waters tested.

Oil and Grease Measurements

Retort waters are co-produced with shale oil and separated from it by decantation and heat treatment. Because of the intimate contact between these two phases, some oil and grease, about 0.1 to 1 weight percent, may remain associated with the water phase (Harding et al., 1978; Fox et al., 1978). A knowledge of the quantity of this material is helpful in overcoming operational difficulties in treatment plants, for assessing environmental impacts of discharged waste, and for assessing the potential of recovering oil and grease. Oil and grease may coat adsorption medium and stripping column packings (Harding et al., 1978; Mercer et al., 1978) and interferes with anaerobic digestion of sludges. If wastewaters containing oil and grease are discharged to receiving waters, they may cause surface films and shoreline deposits, and federal and state laws will require their removal. It may be possible to reclaim oil and grease from retort waters, if sufficient amounts are present.

The purpose of this study is to develop reliable methods to measure amounts of oil and grease in retort waters. We investigated the partition-gravimetric method (*Standard Methods*, 1976) and a Soxhlet extraction procedure (Luthy, 1976) for the measurement of dissolved and suspended oil and grease in retort waters. A number of analytical problems were encountered with these methods, including emulsion formation and water occlusion. Therefore, work was initiated to develop a new method of analysis, based on concentration of hydrophobic material on a reverse-phase chromatographic column and elution with a small quantity of organic solvent. The eluate is further fractionated by passing it through a normal-phase column to remove any polar material.

Standard Analytical Methods. Amounts of oil and grease were initially determined by the partition-gravimetric method outlined in Standard Methods (1976). This method was modified due to analytical problems. The standard method involves acidification of the sample to pH 2, extraction in a separatory funnel with freon, collection and evaporation of the solvent to dryness, and weighing of the residue. Analytical problems encountered include the formation of a precipitate during acidification and an emulsion during freon extraction. The precipitate has been observed by others (Fox et al., 1978) and is hypothesized to be elemental sulfur and organic acids. At this point, it was realized that there were major flaws in the analysis. Occluded water associated with the emulsion would add to the oil and grease determined gravimetrically. Variables affecting the formation of the emulsion were not understood and, therefore, could not be adequately controlled.

Studies were conducted to develop a method for eliminating emulsion formation. A variety of other organic solvents was tried, with and without acidification. It was found that the use of methylene chloride (CH_2Cl_2) without acidification produced the least emulsion. The organic phase could be separated from the water and the small quantity of emulsion. This extraction procedure was used in combination with other separation techniques to measure various fractions of the oil and grease.

Amounts of suspended oil and grease in retort waters were determined by the filtration technique described by Luthy (1976). The suspended oil is important because it represents the fraction of the oil and grease that can be removed from water by coagulation and flotation or by other means. The dissolved fraction, on the other hand, is not affected by these techniques and can only be removed by more expensive solvent-extraction methods.

The sample in Luthy's method was passed through a muslin cloth coated with 100 ml of 10 gm/l Celite filter aid solution. The muslin cloth was supported on a Büchner funnel by a Whatman 40 filter paper. The material collected by the muslin cloth and filter paper was dried with $MgSO_4 \cdot H_2O$ and the residue was placed in a Soxhlet extraction apparatus for 4 hours; it was then extracted with CH_2Cl_2 as noted above. The solvent was collected and evaporated, and the residue dried and weighed to give suspended methylene chloride extractables (SMCE). This fraction, which includes the suspended and emulsified oil, can be removed by coagulation and flotation.

The filtrate from the Celite filtration was extracted by the partition-gravimetric method using CH_2Cl_2. The organic phase, after five extractions, was pooled and taken to dryness. The residue was dried and weighed to give the dissolved methylene chloride extractables (DMCE). Total methylene chloride extractables (TMCE) were determined by adding DMCE and SMCE or:

$$\text{TMCE} = \text{DMCE} + \text{SMCE}$$

Considerable difficulty was encountered with the drying procedure for the organic extracts of the various fractions of oil and grease. The residues gradually lost weight with drying time. The drying procedure was standardized by selecting a drying temperature and time (80°C, 15 minutes).

Table 5 presents the results of suspended and dissolved oil and grease measurements on Occidental and 150-ton retort waters. They show that suspended oil and grease represents much less than half of the total oil and grease in these two retort waters. This is a very significant conclusion because it indicates that coagulation and dissolved air flotation or other similar methods will not effectively remove all oil and grease from retort waters. It also indicates that oil and grease in retort waters are very different from those in conventional wastewaters for which the standard method of measuring oil and grease was developed. These studies indicate that the partition-gravimetric and Soxhlet extraction methods are reproducible when the samples are fractionated by Celite filtration.

Retort waters have high concentrations of carboxylic acids (Fox et al., 1978) which may be extracted during the oil and grease test. These organic acids have different properties than oil and grease, are much less significant environmentally, and may not create a fouling problem in downstream treatment units. Therefore, the significance of the standard oil and grease test and the rationality of environmental

Table 5. Oil and grease determination on 150-ton and Occidental retort water using the partition-gravimetric and Soxhlet extraction methods with methylene chloride and no pH adjustment (mg/l). (Drying temperature was 80°C for 15 minutes).

Occidental	150-ton	
water[a]	retort water	retort
Suspended methylene chloride extractables (Soxhlet Extraction)	354	285 ± 14
Dissolved methylene chloride extractables (Partition-Gravimetric)	1254	467 ± 42
Total methylene chloride extractables	1608	752 ± 77

[a] Average of three replicates

regulations treatment process performance based on it must be questioned. This issue should be investigated in other studies.

Sep-Pak Method of Oil and Grease Analysis. Development of an alternate method of oil and grease analysis is in progress. This new method is being developed to circumvent some of the problems encountered using standard methods and to accelerate the analytical procedure. In this method, amounts of oil and grease were determined by passing a known quantity of sample through a reverse-phase C-18 column (Sep-Pak; Waters and Associates, Milford, Mass.). This column removed the nonpolar fraction (neutral hydrocarbons or the oil and grease fraction) and passed the polar fraction which was discarded. The column was eluted with CH_2Cl_2 after mobile phase switch-over with methanol, and the eluate was dried, taken up in a solvent, and cleaned by passing it through a normal-phase Si Sep-Pak. The Si column removed any residual polar material from the C-18 eluate and passed the non-polar fraction which was collected, dried, and weighed. We used this method to measure amounts of oil and grease in 150-ton retort water and have studied the elution efficiency, breakthrough characteristics, and suitable solvents for the Si Sep-Pak.

As previously noted, the aqueous sample can be treated by Celite filtration. The Celite filtrate is processed through the C-18 and Si columns. The result is an estimate of dissolved hydrophobic material (DHM). An estimate of filterable hydrophobic material, FHM, is obtained as

$$\mathrm{FHM} = \mathrm{THM} - \mathrm{DHM}.$$

One advantage of this approach is that it saves a considerable amount of time. The process of separatory funnel extraction, Soxhlet extraction, and sample drying requires about 60 hours for 20 samples.

Table 6 summarizes the results of oil and grease analyses by reverse-phase column separation only. The results of this test indicate that the C-18 columns may give a facile indication of extractables. The values for THM and DHM bracket those for TMCE and DMCE (Table 5), respectively. The samples for DHM and THM analyses

Table 6. Oil and grease determination on 150-ton retort water using reverse-phase column separation (C-18 Sep-Pak) and methylene chloride extraction with no pH adjustment (mg/l).

Drying Temperature	Dissolved hydrophobic material	Total hydrophobic material	Suspended hydrophobic material (by subtraction)
60°C	2000	2780	780
100°C	560	1300	740

were dried at 60°C and 100°C. The results also demonstrated the influence of drying temperatures on the recovery of oil and grease.

A study of the elution efficiency of the Si Sep-Paks, using CH_2Cl_2 as the eluent, was conducted. A 30-mg oil sample was dissolved in 10 ml of CH_2Cl_2 and the solvent was passed through the Sep-Pak and collected. The Sep-Pak was then eluted with three fresh 10-ml aliquots of CH_2Cl_2 and each eluate was collected separately in a tared pan. The solvent was evaporated from the samples and the residue was weighed. The data show that a single elution with 10 ml of CH_2Cl_2 is sufficient to recover 97 percent of the total mass that could be eluted.

Breakthrough studies were initiated to determine the sorptive capacity of the Si Sep-Pak. Oil samples of various weights were dissolved in CH_2Cl_2 and applied to the Si Sep-Pak. The organic effluent and the eluate from one rinsing with 10 ml of methylene chloride ($C_2H_4Cl_2$) were combined and evaporated to dryness.

There was no evidence that the sorptive capacity of the column had been exceeded up to 130 mg oil. The data indicated that 71 percent of the oil was recovered in the nonpolar fraction, i.e., the fraction that is not retained by the Si Sep-Pak.

The use of different organic solvents with the Si Sep-Pak was investigated. As expected, the partitioning between polar and nonpolar fractions was dependent on the organic solvent used. The recovery percentage of oil and grease increased as the polarity of the solvent increased, in agreement with the eluotropic series. The percentage mass recovered was greatest for CH_2Cl_2 followed by benzene, freon, hexane, and petroleum ether.

The initial results of these studies indicate that Sep-Paks will serve an important function in sample preparation for oil and grease analysis and that liquid chromatography or spectrophotometric methods may be used to obtain valuable data on the composition of the oil and grease fraction.

Electrical Conductivity and pH

Standard Methods (1976) was used to measure conductivity and pH in retort water and gas condensate samples. The relatively high conductivity of these samples required that they be diluted prior to analysis. Measurements were made with a Lab-Line 1100 Mho-Meter. The pH was measured with a Corning 125 pH meter.

TASK 2. PHYSICAL PROPERTIES OF SPENT SHALES

The purpose of this task is to determine the specific surface area, bulk density, and carbon content of spent shales used in the treatability studies. Based on work reported in Task 3, it is recommended that major mineral phases also be determined. To date, surface area measurements have been completed and work is in progress to measure the organic and inorganic carbon content of spent shales. This section will describe the spent shale samples selected for use in this work and the surface area measurements.

Spent Shale Samples

Spent oil shale is the solid residue that remains after the organic material has been extracted from raw shale by pyrolysis. This material is typically light tan to black in color and has little cohesive strength. The elemental composition of spent shale is similar to that of raw shale. Any differences are caused by high temperature mineral and gaseous reactions during the conversion process and by the loss of organics. Since about 20 percent by weight of the raw oil shale is removed during pyrolysis, the concentration of nonvolatilized constituents in the spent shale will be higher than in the raw oil shale by a factor of about 1.3.

The purpose of this program is to investigate the use of both in-situ and surface spent shale for the treatment of in-situ retort waters. In one method, the abandoned in-situ retort would be directly used as a part of a treatment system; water generated in one retort would be circulated through an adjacent spent retort. In a second application, spent shale from a surface retort would be packed in columns and used in a conventional treatment system, much like granular activated carbon columns (Figure 1).

Several surface and in-situ spent shales were selected for evaluation in this work. Pertinent retort operating conditions for each of these spent shales are summarized in Table 7. The four in-situ spent shales were obtained from laboratory retorts operated to simulate in-situ conditions because no field spent shales were available. The samples studied here are from the LLL 125-kg retort (S-14, S-17), the LLL 6000-kg retort (L-1), and the LETC 10-ton retort (S-55). The surface spent shales are from pilot-plant operations of the Lurgi, Paraho, and TOSCO II processes. The elemental characterization of some of these samples is summarized in Table 8.

Surface Area Measurements

We hypothesized that spent shale may be a good adsorbent for organic materials in retort waters based on preliminary experiments in which spent shale removed the color from an organic dye. The surface area of spent shales is important in assessing these adsorptive properties. Residual carbon and internal pores contribute to the surface area of spent shales. When kerogen is removed by pyrolysis, it leaves a network of pores. Additionally, the pyrolysis of kerogen produces not only oil and gas, but also a char or residual carbon. Some processes burn this char for process heat while others, such as TOSCO II, leave it on the spent shale.

Theoretical Considerations. Adsorption is the removal of a component of one phase and its concentration at the interface between two phases. For wastewater treatment, this means the removal of solutes from the aqueous phase (process water) by adsorption on a

Table 7. Retort operating conditions for spent shales evaluated in batch and column studies.

Spent Shale	Retort	Shale Source	Shale Size (cm)	Atmosphere	Maximum Temperature (°C)	Isothermal Advance Rate (m/day)
Simulated in situ processes:						
S-14	LLL 125-kg	Anvil Points, Colorado	0.001-7.6	air/steam	1010	1.6
S-17	LLL 125-kg	Anivl Points, Colorado	1.3-2.5	air/N_2	927	1.7
L-1	LLL 6000-kg	Anvil Points, Colorado	0.001-30 + blocks	air/N_2	995	1.7
S-55	LETC 10-ton	Anvil Points, Colorado	fines - 6	air/steam	650	0.93
Surface retorting processes:						
Lurgi[a]	Lurgi		fines - 0.3	air	530[a]/700[a]	--
Paraho[b]	Paraho direct	Anvil Points, Colorado	0.6-7.6[d]	air	590	--
TOSCO II[c]	TOSCO II	Colony Mine, Colorado	fines-1.3[d]	air	480	--

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[a] Spent shale (from electrostatic precipitator) collected from a Lurgi pilot plant operated for Amoco Oil Co., and described by York (1978). The shale was retorted at 530°C and burned at 700°C.

[b] Collected from the Anvil Points pilot plant operated in the direct mode by J. S. Fruchter. See Fruchter et al. (1979).

[c] Retorted in TOSCO retort and stored in surface disposal pile (exposed to weather) four years prior to experiment. Received from L. Ludlam, Colony Development Co.

[d] Size range is for raw shale feed; spent shale particles are smaller.

Table 8. Elemental composition of spent shales used in this work.

Element	L-1 spent shale[a]	S-14 spent shale[a]	Paraho spent shale[b]	Lurgi spent shale[c]
Al	5.64 ± 0.08*	5.72 ± 0.08*	4.48 ± 0.08*	3.84 ± 0.04*
As	59.6 ± 2.4	62.4 ± 2.4	59.4 ± 1.0	70 ± 2
Ba	748 ± 18	-	604 ± 9	-
C (org)	-	0.12*	-	-
C (inor)	-	0.25*	-	-
Ca	14.3 ± 0.1*	13.4 ± 0.1*	13.3 ± 0.2*	15.6 ± 0.07*
Ce	60.9 ± 0.9	-	51.5 ± 1.5	-
Co	12.9 ± 0.2	-	11.1 ± 0.2	<23
Cr	77.0 ± 1.0	-	44.2 ± 0.9	<67
Cs	6.69 ± 0.17	-	4.68 ± 0.21	-
Cu	58.6 ± 3.4	80.0 ± 3.7	55.9 ± 1.1	43 ± 3
Dy	3.45 ± 0.10	-	3.5 ± 0.2	-
Eu	0.894 ± 0.013	-	0.73 ± 0.02	-
Fe	3.11 ± 0.06*	3.20 ± 0.08*	2.40 ± 0.03*	2.06 ± 0.02*
Ga	12.6 ± 1.6	15.5 ± 1.7	11.6 ± 1.2	10 ± 2
Ge	1.6 ± 1.2	<2.1	-	1.9 ± 1.2
Hf	2.72 ± 0.06	-	2.11 ± 0.03	-
Hg	0.0011 ± 0.0004	-	0.035 ± 0.003	<3
K	2.34 ± 0.03*	2.48 ± 0.03*	1.86 ± 0.03*	1.44 ± 0.02*
Mg	5.37 ± 0.10*	5.33 ± 0.10*	4.07 ± 0.06*	4.50 ± 0.06*
Mn	490 ± 10	-	396 ± 14	431 ± 24
Mo	30.6 ± 2.5	-	33.7 ± 1.3	-
Na	2.41 ± 0.02*	2.51 ± 0.26*	2.19 ± 0.03*	1.71 ± 0.10*
Ni	33.2 ± 4.4	49.5 ± 5.0	32.1 ± 1.5	28 ± 4
Pb	62.0 ± 2.5	74.7 ± 2.9	36.2 ± 2.0	28 ± 2
Rb	100 ± 4	104 ± 4	88.4 ± 1.8	83 ± 3
Sb	3.16 ± 0.20	-	2.63 ± 1.5	-
Se	2.2 ± 0.8	2.1 ± 0.8	2.3 ± 0.1	4.9 ± 0.8
Si	21.4 ± 0.1*	21.8 ± 0.1*	18.2 ± 0.4*	14.9 ± 0.1*
Sr	1020 ± 40	965 ± 38	879 ± 12	1140 ± 50
Th	9.86 ± 0.07	-	7.55 ± 0.10	7 ± 2
Ti	0.21 ± 0.05*	0.26 ± 0.01*	0.24 ± 0.01*	0.17 ± 0.01*
U	7.19 ± 0.06	-	5.10 ± 0.14	5.6 ± 2.4
V	152 ± 21	-	129 ± 6	-
Zn	173 ± 6	165 ± 6	82.3 ± 2.2	97 ± 4

* Percent

[a] Fox, 1980

[b] Fruchter et al., 1979

[c] Measured in this study

solid surface (spent shale). The efficiency of this process depends on the nature of the solute and the nature of the adsorbent.

There are different types of adsorption mechanisms. Chemisorption involves an interaction between a compound or a functional group with a specific site on the surface, while ion-exchange involves electrostatic attraction between an ionic solute and a charged surface. Both of these mechanisms require affinity by the solute for the surface. Hydrophobic solutes are also adsorbed on a surface because of the free energy release when such a solute is removed from solution. In this case, the solute is bound to the surface by van der Waals forces, and the interaction is relatively non-specific. The adsorption of components in retort water onto spent shale will probably involve all three mechanisms operating simultaneously.

The surface area of the adsorbent is an important parameter in all three types of adsorption. The high surface area of spent shale results from char and pores left after the removal of kerogen during retorting. The pore-size: pore-volume distribution is also important because, if the pore diameter is too small, certain compounds may be sterically excluded from the surface within the pores or the diffusion of solutes into these pores may be slow. If a large fraction of the pore volume of spent shale is in pores of small diameter, the efficiency of adsorption will be reduced.

Experimental. The surface area of spent shale was determined by using a Quantsorb BET apparatus. The operating principle is based on work that was done on multimolecular layer adsorption of gases performed by Brunauer, Emmett, and Teller (1938).

In the BET apparatus, the sample is placed in a U-shaped tube and a continuous flow of helium and nitrogen gas mixture is passed over it. The sample is then cooled to liquid nitrogen temperatures where the nitrogen gas is readily adsorbed onto the surface while the helium, the carrier gas, is not. When adsorption is complete, the nitrogen is desorbed by raising the tube temperature to room temperature in a water bath. The adsorption and desorption of nitrogen are monitored by a thermal conductivity detector.

The surface area was estimated from the Brunauer, Emmett and Teller equation:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{P}{P_o}$$

where P = pressure of gas adsorbed

P_o = total pressure = carrier gas and adsorbed gas

V = volume of adsorbed gas

V_m = volume of gas for monolayer formation

C = constant related to the heat of adsorption and heat of liquefaction

by determining V_m graphically from a plot of

$$\frac{P}{V(P_o - P)} \text{ vs } \frac{P}{P_o}$$

and the size of nitrogen gas molecules.

Results and Discussion. The surface area measurements of the six spent shales were compared with activated carbon and surface areas computed from equivalent diameter spheres (Table 9). Since the surface areas of equivalent diameter spheres were two orders of magnitude lower than the measured surface area, the measured surface area must be due to internal porosity. This is consistent with results reported by Burnham (1979a) and Slettevold et al. (1978). Measurements of two or more particle size ranges for the surface retorted shales indicated that, except for Lurgi spent shale, the surface area was practically independent of the particle size. This suggested that there is little inaccessible internal porosity, in agreement with Burnham's (1979a) findings. Results from measuring TOSCO II spent shale were different from the others studied: surface area was dependent on particle size and the surface area increased for larger particles. The cause of this behavior is not known.

The effect of retorting temperature on surface area is shown in Figure 8, which indicates that surface area decreases as the retorting temperature increases. This trend is difficult to interpret because a number of other variables, including carbon content of the spent shale and isothermal advance rate, may affect final surface area. Burnham (1979a) showed that residual carbon may make a significant contribution to spent shale surface area in samples that are not decharred. Burnham (1979b) also indicated that the surface area of residual carbon in spent shales ranges from 284 to 404 m^2/g as determined by CO_2 adsorption (Burnham, 1979b). Although residual carbon measurements are not available for the samples studied here, it is known that

Table 9. Specific surface area of spent shales determined by N_2 adsorption.

Sample	Particle Size Range (μm)	Specific Surface area	Specific Surface Area for sphere[a] (m^2/g)
Powdered Activated Carbon	45	1000–1100	0.053
Surface retorted			
Paraho	<63	3.50	>0.038
	63–250	3.37	0.010–0.038
Lurgi	<63	4.76	>0.038
	63–250	4.77	0.010–0.038
TOSCO II	<63	6.63	>0.038
	63–250	9.20	0.010–0.038
	>250	10.19	<0.010
Simulated In-Situ			
L-1	<250	2.10	>0.010
S-14	63–250	2.40	0.010–0.038
S-55	<300	4.20	>0.008

[a] Estimated for a sphere with a diameter equivalent to the particle size range and a density of 2.5 g/cm^3 from $S_W = 6/(\text{density} \times \text{diameter})$, after Stettevold et al., 1978.

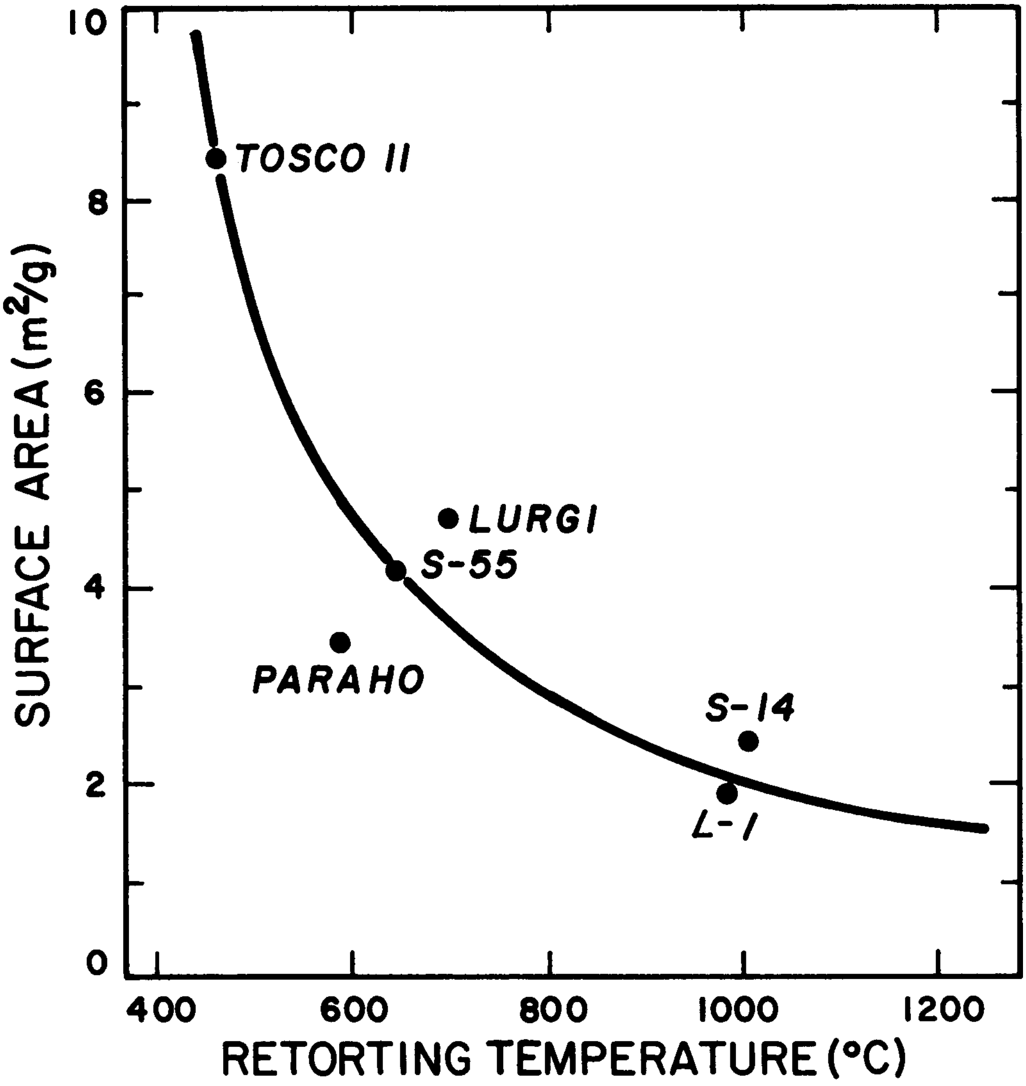

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Figure 8. Relationship between retorting temperatures and spent shale surface area.

the majority of the residual carbon was burned off of all of these spent shales except TOSCO II and Lurgi. The L-1, S-14, S-55, and Paraho spent shales were produced by combustion retorting, and residual carbon was partially burned to supply process heat. The majority of the residual carbon was burned off of the LLL in-situ spent shales (L-1 and S-14), which have the lowest surface areas. The surface areas measured by Burnham (1979a) by N_2 adsorption for decharred spent shales by the BET method, 2.1 and 2.8 m^2/g, are very close to the values measured here for L-1 and S-14 spent shales, 2.1 and 2.4 m^2/g.

TASK 3. BATCH STUDIES

The purpose of this task is to screen several shale-water combinations to determine the potential of spent shale for the treatment of oil shale process waters. Initially, the studies were to focus on organic carbon and electrical conductivity. However, preliminary experiments indicated that spent shale significantly reduced the inorganic carbon and elevated the pH of retort water. Since these results were very significant for the treatment of retort waters, the scope of the program was enlarged to include pH and inorganic carbon.

This task was to be carried out by conducting "preliminary" and "isotherm" batch experiments. The purpose of the preliminary batch experiments was to determine the time required to reach equilibrium and to screen several shale-water combinations. The most favorable shale-water combination would be selected for further testing in the isotherm batch studies. The purpose of these latter studies was to develop isotherms for use in designing the column experiments.

The preliminary and isotherm batch experiments are in progress and have demonstrated that spent shale reduces the organic and inorganic carbon and conductivity and elevates the pH of process waters. The results of these experiments are described below.

Preliminary Batch Studies

The purpose of these studies was to develop experimental procedures and to screen several shale-water combinations. Initially, optimum experimental conditions were determined by contacting various weights of shale and water for various times. Experimentation with the liquid-solids ratio indicated that approximately 50 ml of water per 50 g of shale was necessary to observe measurable amounts of adsorption. At much lower shale-water weight ratios, organic carbon was leached from the spent shale, rather than being adsorbed onto it. Since a 1:1 ratio simulates conditions that would be found in a packed bed, this ratio was selected for all further testing.

Studies were also conducted to determine the time required before equilibrium was reached. The results of studies conducted for Lurgi and Paraho shales and Omega-9 retort water are summarized in Figure 9 which indicates that, within the limits of experimental error, there is no change in organic carbon after 48 hours of contact with spent shale. Based on these studies, 120 hours was selected as a very conservative equilibrium time for all batch studies.

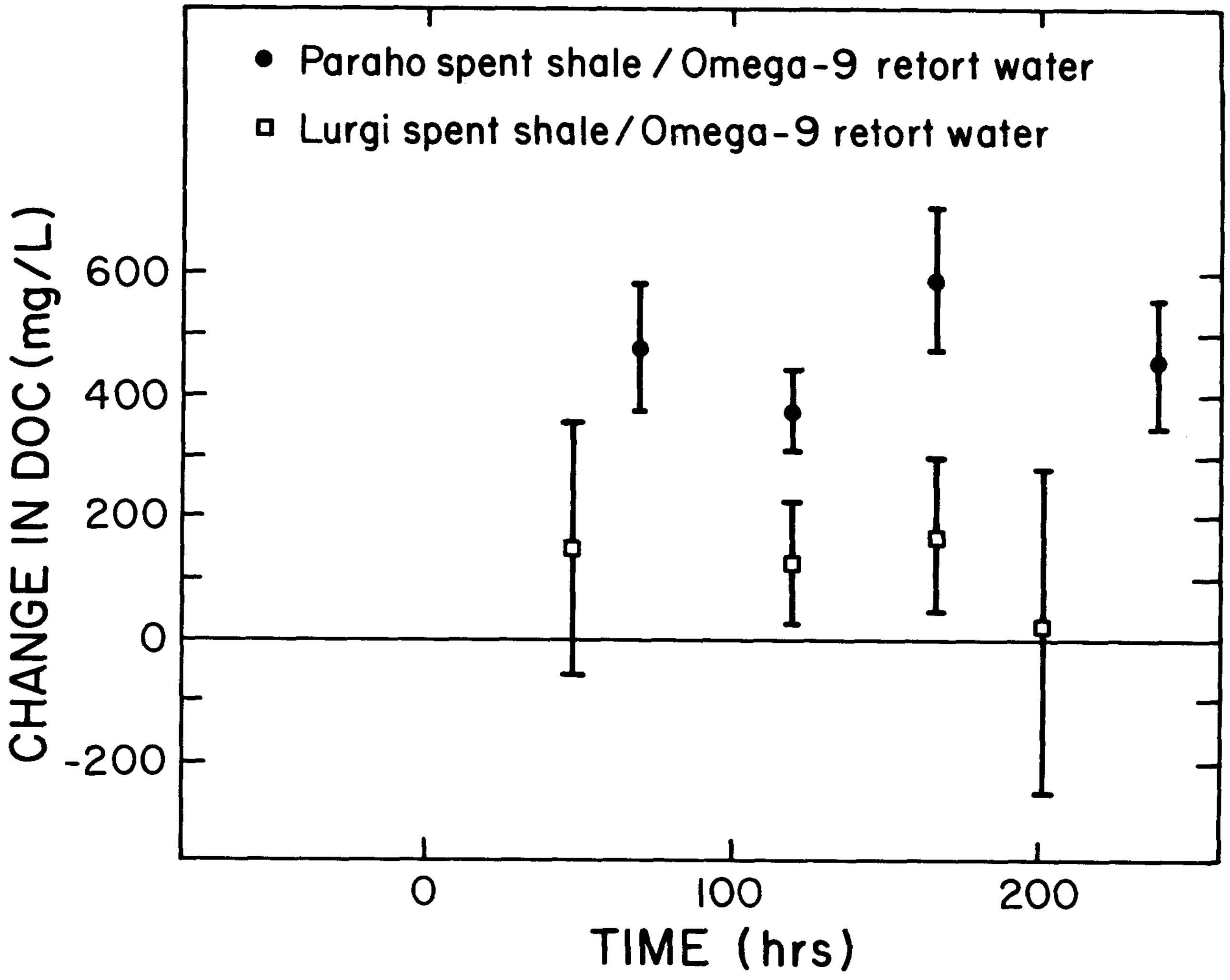

Figure 9. Equilibrium time studies.

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Subsequently, all batch studies were conducted using 50 g of spent shale and 50 ml of process water contacted for 120 hours. The shale and water were placed in 250-ml Erlenmeyer flasks and the flasks were sealed using parafilm-wrapped ground-glass stoppers. Sealed flasks were placed on a mechanical shaker for various amounts of time. Samples were obtained by filtering the entire supernatant and much of the slurried solids through a 0.45 μm Millipore filter.

The effect of spent shale treatment on dissolved organic and inorganic carbon, electrical conductivity, and pH in several process waters is summarized in Table 10. The specific adsorption ranged from 0.00 to 1.6 mg organic carbon per gram of shale. TOSCO II is the best adsorbent for organic carbon in the waters investigated, followed by Paraho spent shale. The remaining four shales, Lurgi, L-1, S-14, and S-55, are as much as an order of magnitude poorer in organic adsorptive capacity than the TOSCO II and Paraho samples. The percent reduction in organic carbon ranged from near zero for in-situ spent shales to 66 percent for TOSCO II shale and was lower for spent shales retorted at high temperatures than for shale retorted at low temperatures (Figure 10). This effect is due to the decrease in surface area of spent shales at higher temperatures (Figure 8). There was a positive correlation between surface area and adsorption for all spent shales except Paraho. Paraho spent shale, with a relatively small specific surface area, is one of the best organic adsorbers. This suggests that the chemical nature of the spent shale surfaces may be significantly different.

Table 10. Specific adsorption of organic carbon and percent change in organic carbon, inorganic carbon, electric conductivity, and pH of process water after 120 hours of contact with spent shale in batch experiments using 50 g shale and 50 ml process water.

			PERCENT CHANGE[a]					
			Surface spent shales			In-situ spent shales		
	Parameters measured in process water	Initial concentrations (mg/l)	Paraho	Lurgi	TOSCO II	L-1	S-14	S-55
Omega-9	Organic carbon	915	-49/0.44[c]	NS[b]	---[d]	-18/0.18[c]	NS/0.10[c]	-12/0.11[c]
	Inorganic carbon	3450	-91	-98	--[d]	-98	-98	-98
	Electrical conductivity	26,200	-28	-6	--[d]	-20	--	-31
	pH	8.78	+116	+119	--[d]	+131	--	+136
150-ton	Organic carbon	3300	-24/0.82[c]	NS/0.12[c]	-48/1.6[c]	NS/0.12[c]	NS/0.09[c]	-7/0.23[c]
	Inorganic carbon	6400	-89	-97	-60	-98	-97	-98
	Electrical conductivity	36,000	-40	--	NS	-36	--	-54
	pH	8.80	+111	+110	NS	+116	---	+119
L-2 retort water	Organic carbon	1675	-51/0.89[c]	-17/0.30[c]	-66/1.1[c]	-13/0.22[c]	NS/0.00[c]	-18/0.29[c]
	Inorganic carbon	6660	-89	-96	-47	-97	-98	-98
	Electrical conductivity	38,100	-54	--	--	-60	--	-60
	pH	8.66	+117	+109	--	+126	--	+123
L-2 gas condensate	Organic carbon	1300	-45/0.57[c]	-21/0.27[c]	-27/0.95[c]	-11/0.16[c]	NS/0.10[c]	NS/0.07[c]
	Inorganic carbon	3640	-91	-93	-65	-97	-99	-97
	Electrical conductivity	24,100	-49	--	--	-54	--	-75
	pH	9.20	+111	+113	--	+121	--	+127

[a] A negative value indicates that the concentration was reduced by the indicated amount while a positive value indicates an increase in the process water.

[b] No statistically significant change.

[c] Specific adsorption in mg DOC/g shale.

[d] TOSCO II was also evaluated with Geokinetics retort water. The specific adsorption for this combination was 1.3 mg/g and the inorganic carbon reduction was 83 percent. Changes in pH and conductivity were not significant.

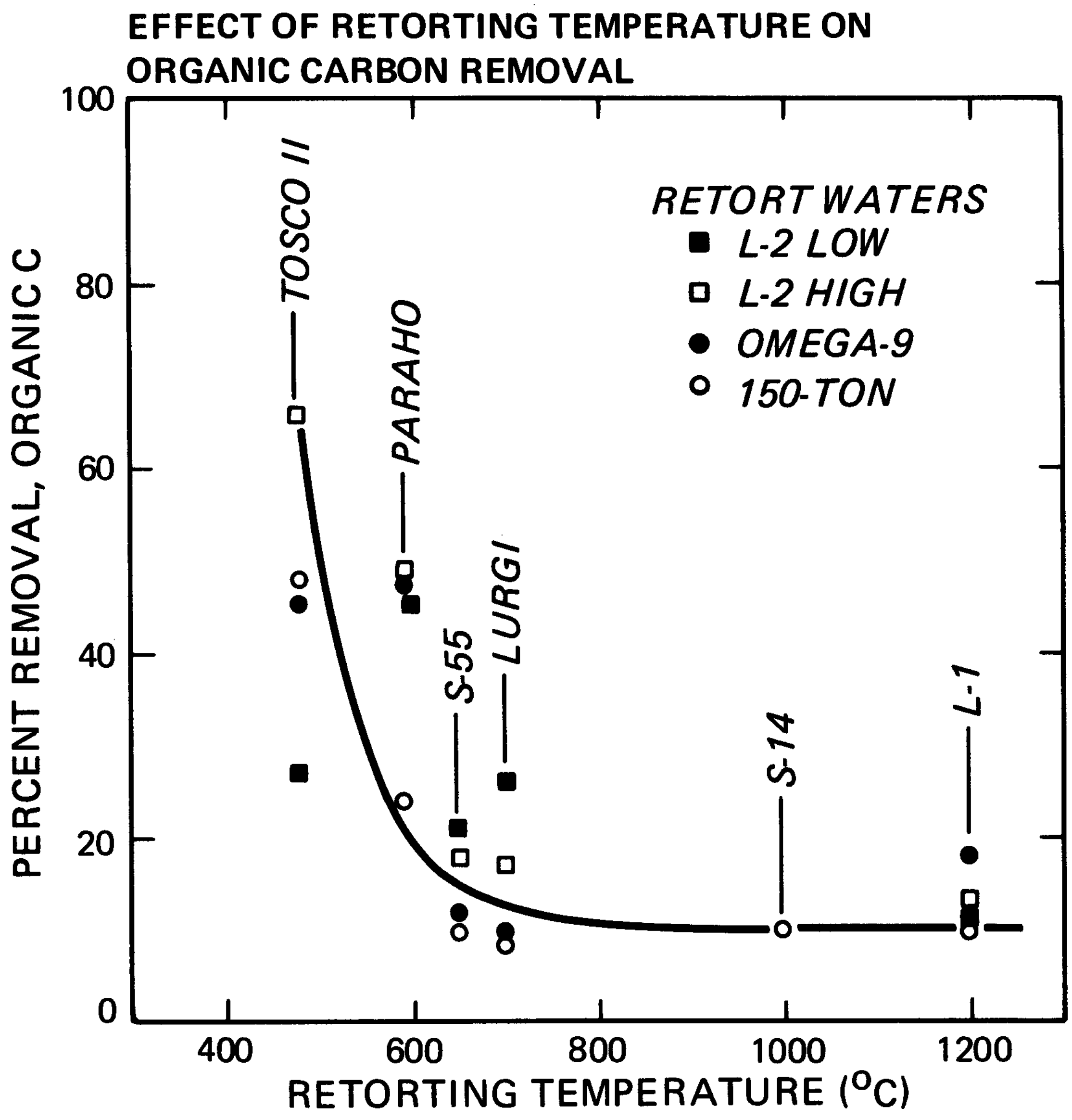

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Figure 10. Effect of retorting temperature on the removal of organic carbon from process waters.

The data in Table 10 also indicate that the amount of organic carbon adsorbed from solution is not controlled merely by the concentration of organic carbon remaining in the water nor by saturation of the shale's adsorptive capacity, but that the amount adsorbed is also a function of the chemical nature of the solute. Paraho shale, for example, adsorbs neither a consistent weight nor a consistent percentage of organics from the four process waters. This suggests that some components are adsorbed preferentially and that the organic composition of these waters varies.

Spent shale may also remove up to 98 percent of the dissolved inorganic carbon from process water samples. The percent reduction increases almost linearly up to 700°C and levels off to 98 percent at higher temperatures (Figure 11). Spent shales with the highest organic adsorptive capacity appear to be least effective in removing inorganic carbon. Thus, Paraho and TOSCO II spent shales cause the least inorganic carbon reduction and the remaining spent shales, Lurgi, L-1, S-14, and S-55, are the most effective in this respect. The reason for the inverse relationship between organic and inorganic carbon percent reduction is unknown and is certainly related to different mechanisms.

The reduction in inorganic carbon is hypothesized to be due to precipitation or ion exchange reactions between the carbonate species in process water (Table 2) and hydroxides formed from the hydration of CaO and other metal oxides in spent shale. This type of reaction can be summarized by the following equations:

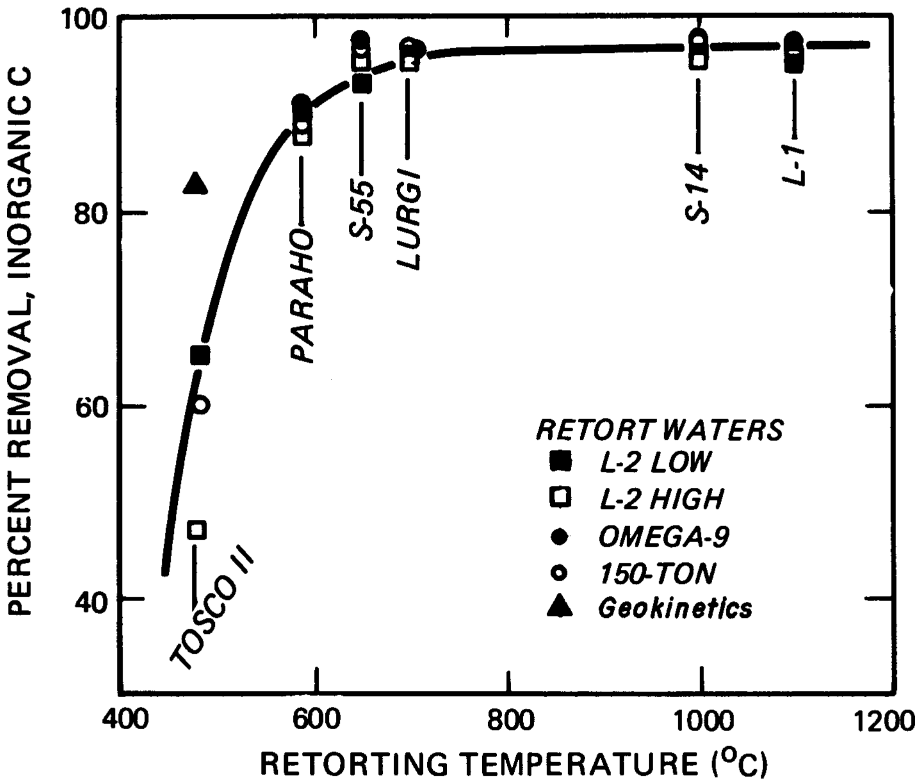

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Figure 11. Effect of retorting temperature on the percent removal of inorganic carbon from process waters.

$$Ca(OH)_2 + HCO_3^- \longrightarrow CaCO_3 + H_2O + OH^-$$

$$(Ca_xSi_yO_z)\cdot 2OH^- + HCO_3^- \longrightarrow (Ca_xSi_yO_z)\cdot CO_3^= + H_2O + OH^-$$

This type of mechanism is consistent with the effect of spent shales on electrical conductivity and pH. The batch studies demonstrated (Table 10) that the reduction in inorganic carbon is accompanied by a decrease in electrical conductivity and an elevation in pH from initial levels of 8 to 9 to final levels of 10 to 11. The decrease in conductivity is due to the removal of dissolved inorganic carbon (i.e., CO_3, HCO_3) from the water. The increase in pH is due to the release of OH when hydrated metal species react with HCO_3. Although not measured here, the increase in pH would convert ammonium (NH_4) to ammonia (NH_3), which could be stripped from the waters on passage through a column.

Because the adsorption of organics (Table 10) was lower than anticipated, a series of experiments was conducted to determine if the adsorptive properties of spent shales could be improved by chemically or physically treating the shale. This approach was selected because the net surface charge of a solid and the charge of ions in solution both determine the degree of adsorption possible. Additionally, Slettevold et al. (1978) had demonstrated that acid leaching of spent shales increases their surface area.

Many hydrated solids have a pH at which the number of positive and negative surface charges are equal. In spent shale, for example, such groups would include Ca^{++}, $Si^{-}O^{-}$, and any adsorbed ions. Above this pH, the net surface charge is negative; and below, it is positive. The surface charge is quite important to the adsorption of polar organics in retort waters. In particular, a highly negative surface would inhibit the adsorption of aliphatic acids and phenols at the high pH encountered in retort water. A pH of 5 is calculated to be the zero point of charge for acid-leached 150-ton shale. Pretreatment of both shale and water is required to reach and maintain acidic conditions.

Acid leaching of the spent shale and pH modification of the water were investigated as means to improve the adsorptive capacity of spent shale. Fifty grams of S-17 and 150-ton spent shale were contacted with 100 ml of 6 N HCl for 24 hours and washed with distilled water. The pH of 100 ml of 150-ton retort water was modified by contacting it with 50 g of S-17 spent shale for 24 hours, filtering, and sparging to remove NH_3. The pH was then adjusted from 12 to 5 and the sample again sparged to remove CO_2. A pH of 5 was used because this is the isoelectric point (the zero point of electric charge) for acid-leached shale.

The water and shale resulting from these treatments were used in batch studies and the results compared to those from similar batch studies using untreated samples. The results of these investigations are shown in Table 11, which indicates that there is no statistically

Table 11. Effect of acid leaching of spent shale and pH adjustment of retort water on specific adsorption of dissolved organic carbon from 150-ton retort water.

shale Spent Shale	Specific Adsorption mg DOC/g	
	Treated[a]	Untreated
150-ton	1.0 ± 0.3	1.0 ± 0.3
S-17	0.4 ± 0.3	0.0 ± 0.2

[a] Shales contacted with 100 ml of 6N HCl for 24 hours and washed with distilled water. Retort water (100 ml) contacted with 50 g S-17 spent shale for 24 hours, sparged, pH adjusted to 5, and resparged.

significant difference between the treated and untreated samples. Based on these negative results, this line of investigation was abandoned, and no further spent shale treatment studies conducted.

Isotherms

A single isotherm study for dissolved organic carbon was conducted using Paraho spent shale and Geokinetics retort water. This study revealed that conventional techniques used to develop isotherms have limited applications in the spent-shale retort-water system. Liquid-solid ratios less than 1.5 ml/g create slurries that cannot be dewatered. An alternate technique was investigated to overcome this problem. Isotherms developed using the conventional (A) and alternate (B) technique are shown in Figure 12.

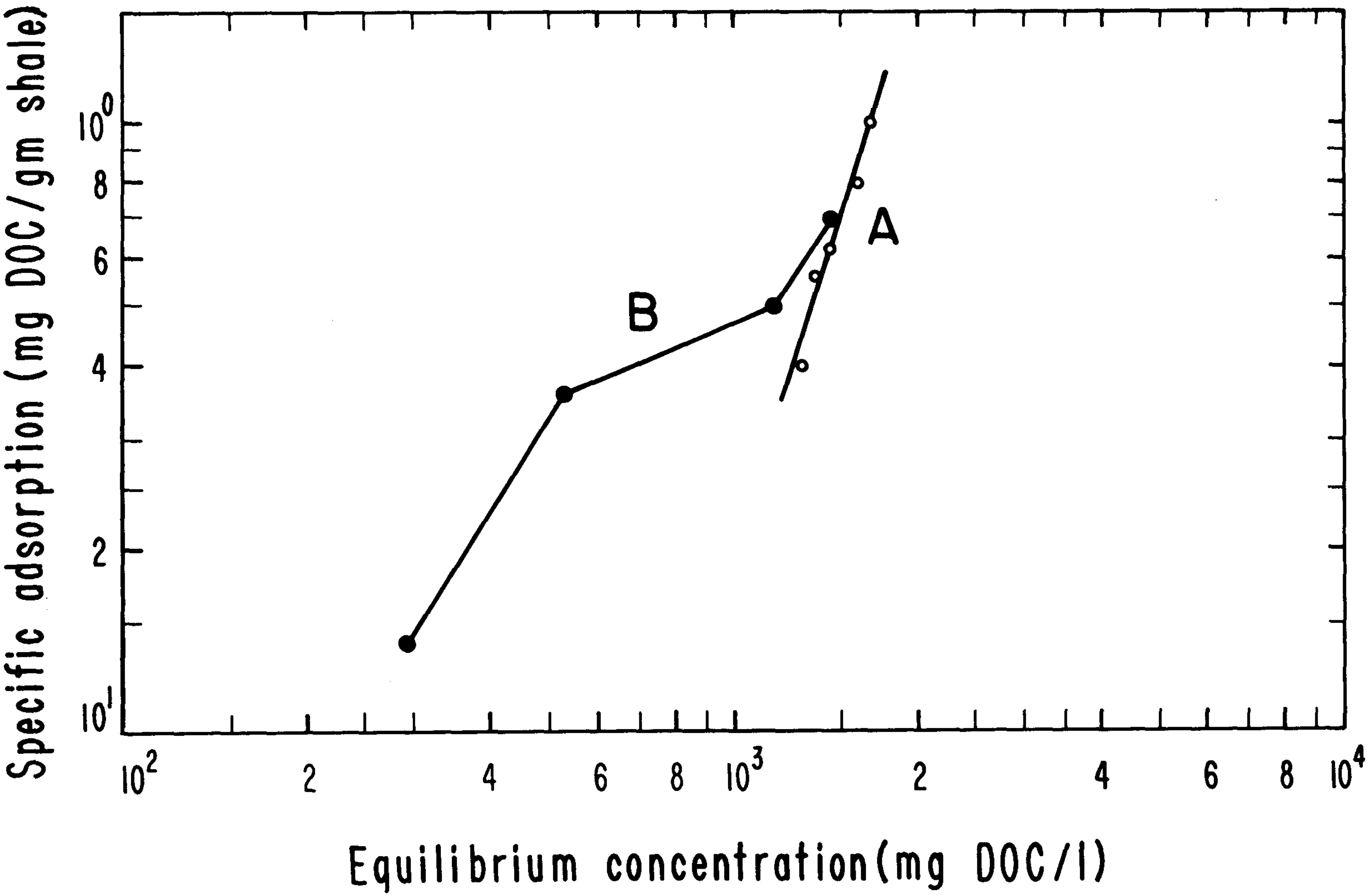

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Figure 12. Dissolved organic carbon (DOC) isotherm for Paraho spent shale and Geokinetics retort water.

Batch adsorption studies are normally carried out by varying the quantity of adsorbent (spent shale) in the presence of a fixed quantity of liquid (retort water), thus changing the liquid-to-solid ratio without altering the initial concentrations and composition of adsorbates under study. Isotherm A (Figure 12) was obtained in this way. This isotherm is incomplete because liquid-to-solid ratios in excess of 75 ml of Geokinetics water to 50 g of Paraho spent shale create slurries that cannot be dewatered. The equilibrium concentration of organic carbon did not fall below 1200 mg/l for this spent-shale retort-water combination. The high concentration of organic carbon remaining in solution at equilibrium and the constraint on solid addition imposed by intractable paste formation limited the development of the adsorption isotherm.

An alternative approach was therefore tested by interchanging variables in order to eliminate the problem of paste formation and to complete adsorption isotherm development. The liquid-to-solid ratio was held constant and the equilibrium concentration was varied by diluting the retort water. This approach also presents problems as it assumes that the initial concentration has no effect on the adsorption process, an invalid assumption as the rates of adsorption are dependent on the initial concentration gradient. Isotherm B was developed using this technique.

The steep slope of adsorption isotherm A indicates that Paraho spent shale may not be effective for removing dissolved organic carbon. However, spent shale columns may be useful for removing specific organic compounds or classes of organic compounds.

Samples obtained from the batch studies of Paraho spent shale and Geokinetics water were also examined by gas chromatography (GC) to develop specific compound isotherms. The results of these analyses are shown in Figures 13 and 14. For purposes of this analysis, a GC peak was treated as a single species or compound (such a peak may be a mixture of organic species with similar retention times). By plotting percent peak height adsorbed per gram of shale against the percent of the initial peak remaining after adsorption, a concentration-related isotherm was obtained. These data clearly indicate the preferential adsorption of some classes of organic compounds. Note that these isotherms indicate desorption of some components and hence, competition between species for adsorption sites.

TASK 4. COLUMN STUDIES

The purpose of the column studies is to determine spent shale performance and design criteria. Contact time, bed depth, pretreatment requirements, spent shale dosage, breakthrough characteristics, and headloss will be determined.

A single preliminary column experiment was conducted during the study period. Based on the result of this experiment, larger-scale column experiments will be run in FY 1980. In this experiment, 253.5 g of Paraho spent shale were packed into a 230 ml, 1 inch diameter glass Altex chromatographic column. The column was operated in an upflow configuration, and Geokinetics water was pumped through the column at a nominal flow rate of 5 ml/hr using a Sage model 375A peristaltic pump. Problems were encountered with column plugging and failure of

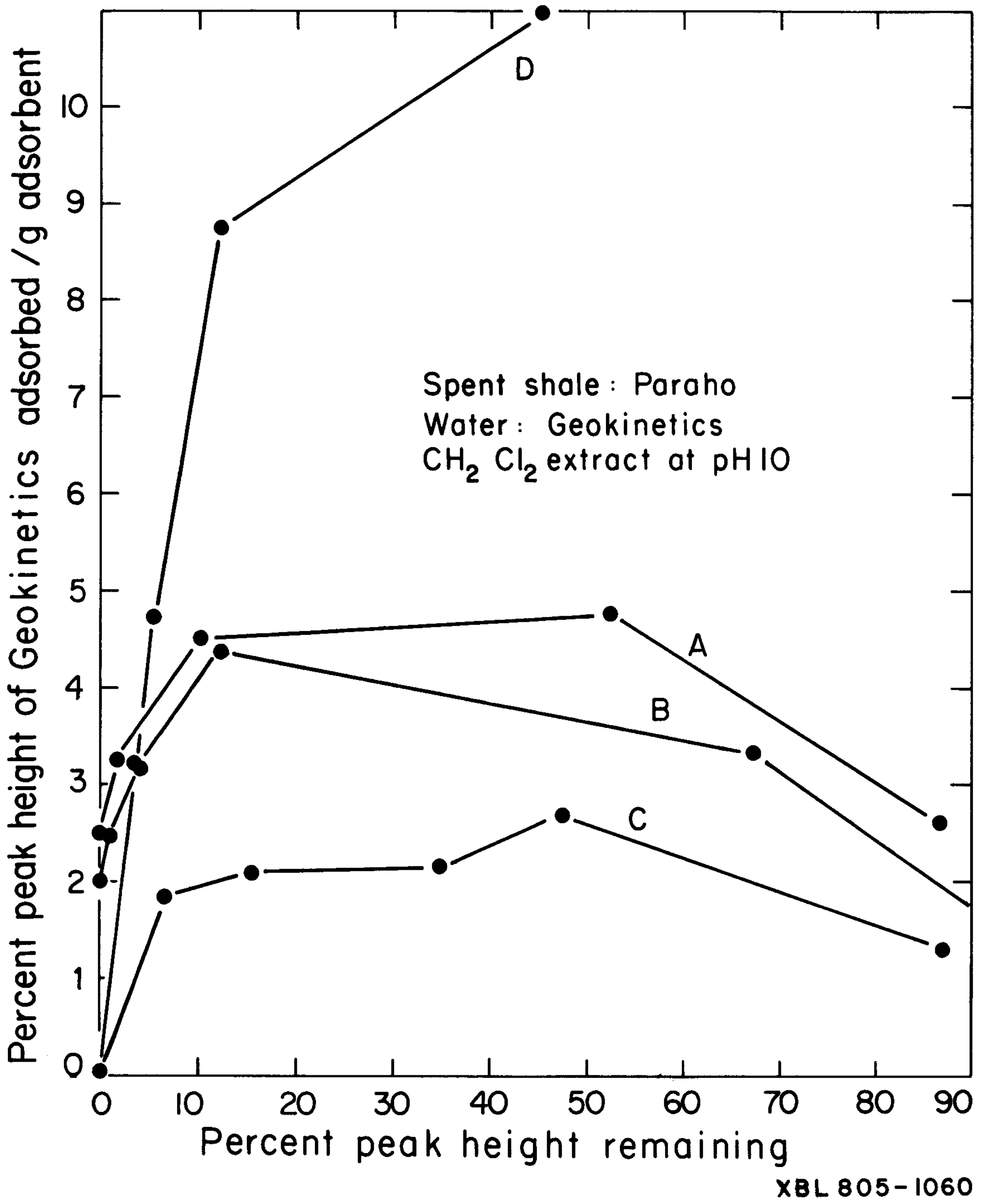

Figure 13. Single compound isotherms for unidentified compounds A-D and E using Paraho spent shale and Geokinetics retort water.

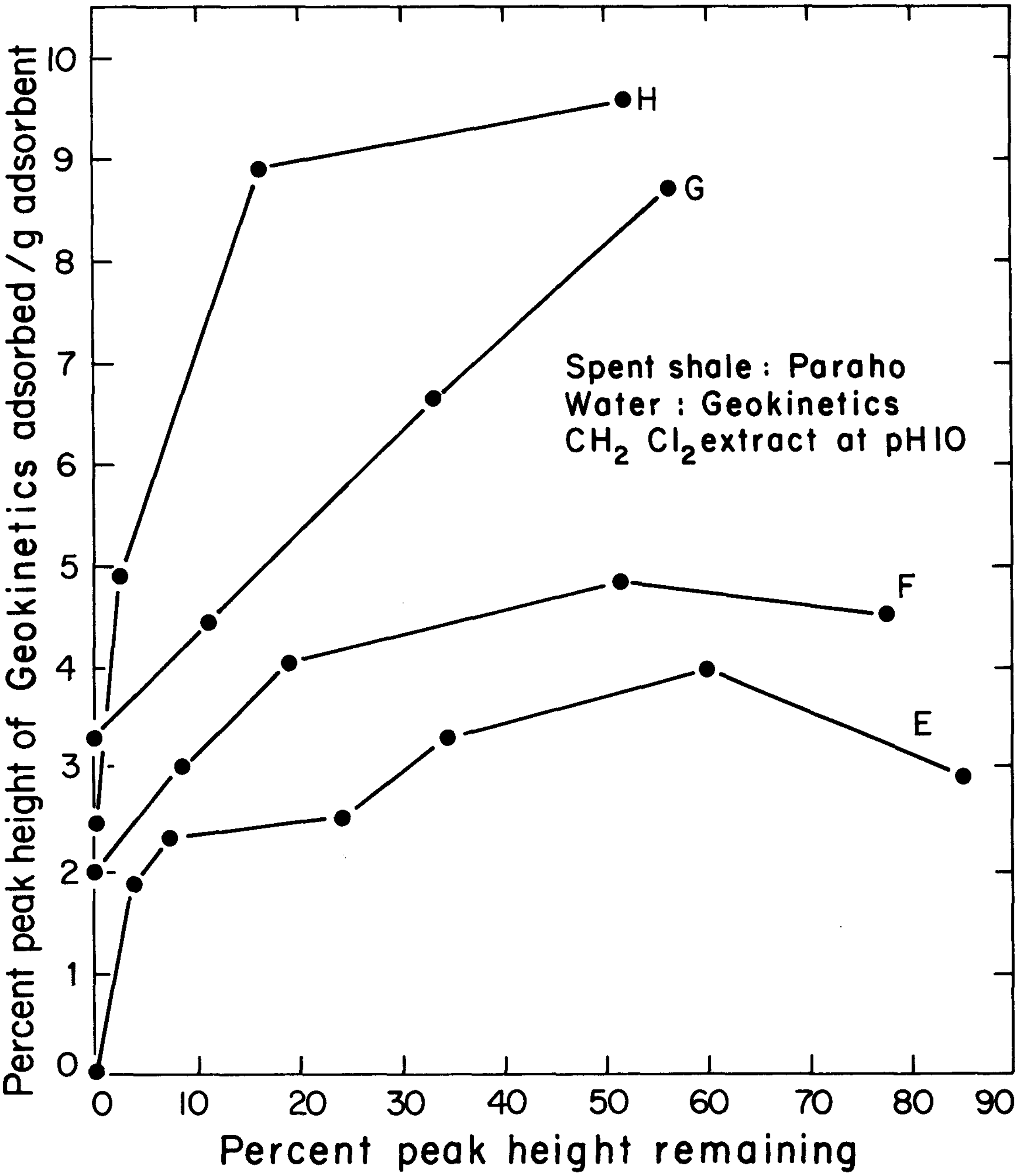

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Figure 14. Single compound isotherms for unidentified compounds E-H using Paraho spent shale and Geokinetics retort water.

tubing connections under pressure. Paraho spent shale was chosen for the study because TOSCO II spent shale, which is the better adsorbent, was not available at the time of the investigation. The column influent and effluent were characterized spectrophotometrically and by gas chromatography. Dissolved organic and inorganic carbon, electrical conductivity, pH, and absorbance measurements at 215 and 260 nm are summarized in Figures 15 and 16.

This study indicated that spent shale adsorption in the column mode may not be effective for removing gross organics (dissolved organic carbon) because column breakthrough occurs before two pore volumes can be treated. This is consistent with previously reported results of the batch studies. Operation and maintenance costs of a spent shale column could be excessive. However, spent shale treatment using slurry techniques may be feasible or columns may be useful for removing specific organic compounds or classes of organic compounds or for reducing color and odor.

The characteristic color and odor of retort water was almost completely removed by the spent shale column. This may be related to the removal of organic components responsible for the color and odor of these waters.

The nature of the specific organic compounds removed by columns of spent shale was investigated spectrophotometrically and by gas chromatography (GC). Retort waters were extracted at alkaline and acidic pH before injection into the GC. Twenty-five ml of sample were extracted with two 15-ml portions of methylene chloride. The organic

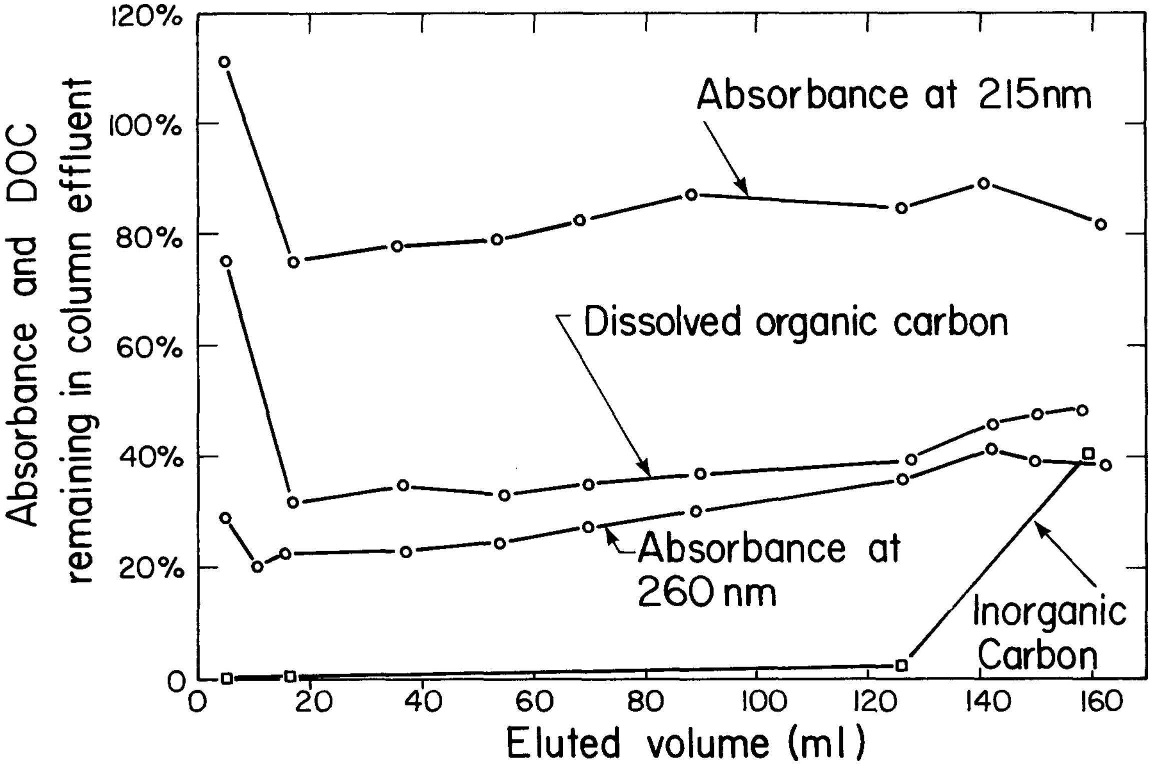

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Figure 15. Effect of column of Paraho spent shale on organic and inorganic carbon in Geokinetics retort water (column pore volume = 86 ml).

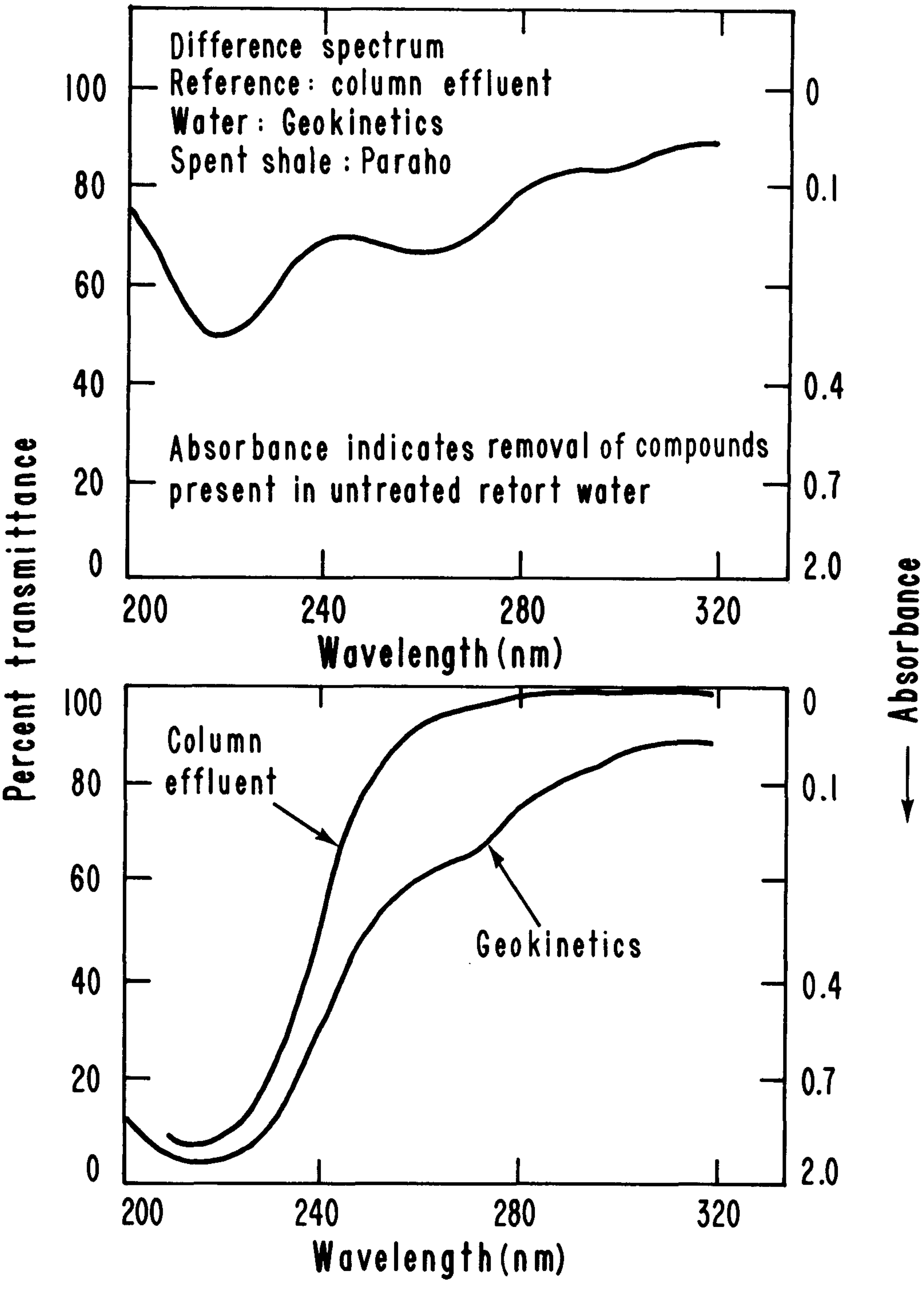

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Figure 16. Difference spectrum for adsorption of organics from Geokinetics retort water on Paraho spent shale.

fraction was dried over anhydrous Na_2SO_4 and then evaporated under dry nitrogen to approximately 1 ml. In an effort to minimize the loss of volatile constituents, no attempt was made to control solvent cooling that occurred during evaporation. The CH_2Cl_2 fraction was added to 5 ml of heptane and the mixture evaporated to a total volume of 5 ml in a stream of nitrogen. No insoluble residues were detected. Four microliters of the heptane extract were injected into a 1/4 inch diameter column packed with 5 percent Carbowax 20M TPA on Chromosorb W. The carrier gas was high purity helium at a flow rate of 40 cc/min. A flame-ionization detector was used.

The GC work coupled with the data shown in Figures 17 and 18 indicate a dramatic depletion of the methylene chloride extractable components in retort water during spent shale treatment. Figure 17 shows the complete removal of basic extractables while Figure 18 shows only one major peak remaining in the acid extract. This not only demonstrates the effectiveness of spent shale as an adsorbent for at least some of the organic contaminants in retort water, it also indicates that the 30 to 40 percent of the organic carbon that is not adsorbed is the most polar and soluble fraction of the organics. This is predictable since non-specific adsorption is inversely related to solubility. Thus, it can be expected that those compounds that are least soluble in water will be removed most easily from aqueous solution by adsorption onto spent shale.

TASK 5. SYSTEM STUDIES

The purpose of this task is to interface spent shale treatment with a complete treatment system. The batch and column studies

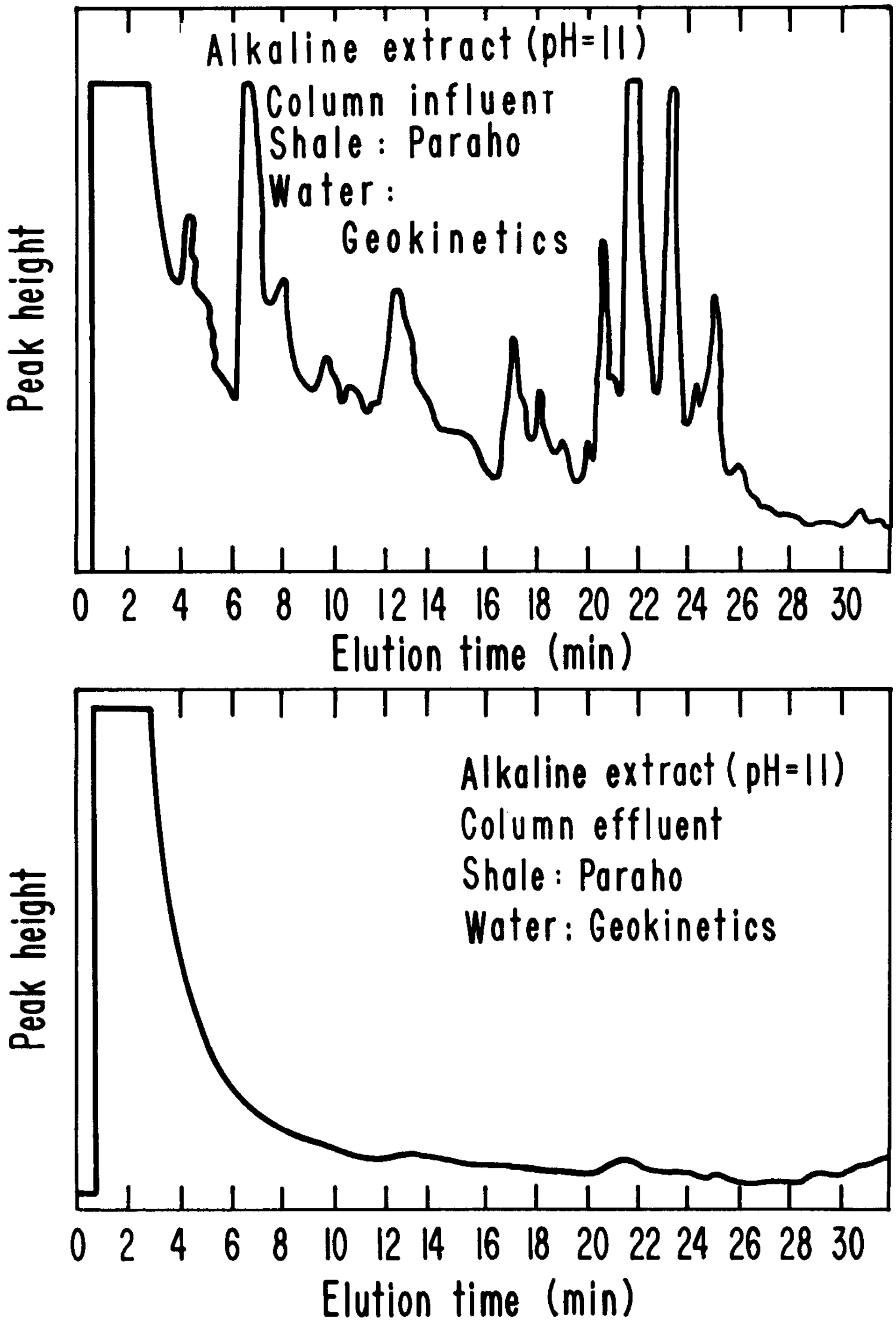

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Figure 17. Gas chromatography fingerprints of alkaline extracts of Paraho/Geokinetics column influence and effluent.

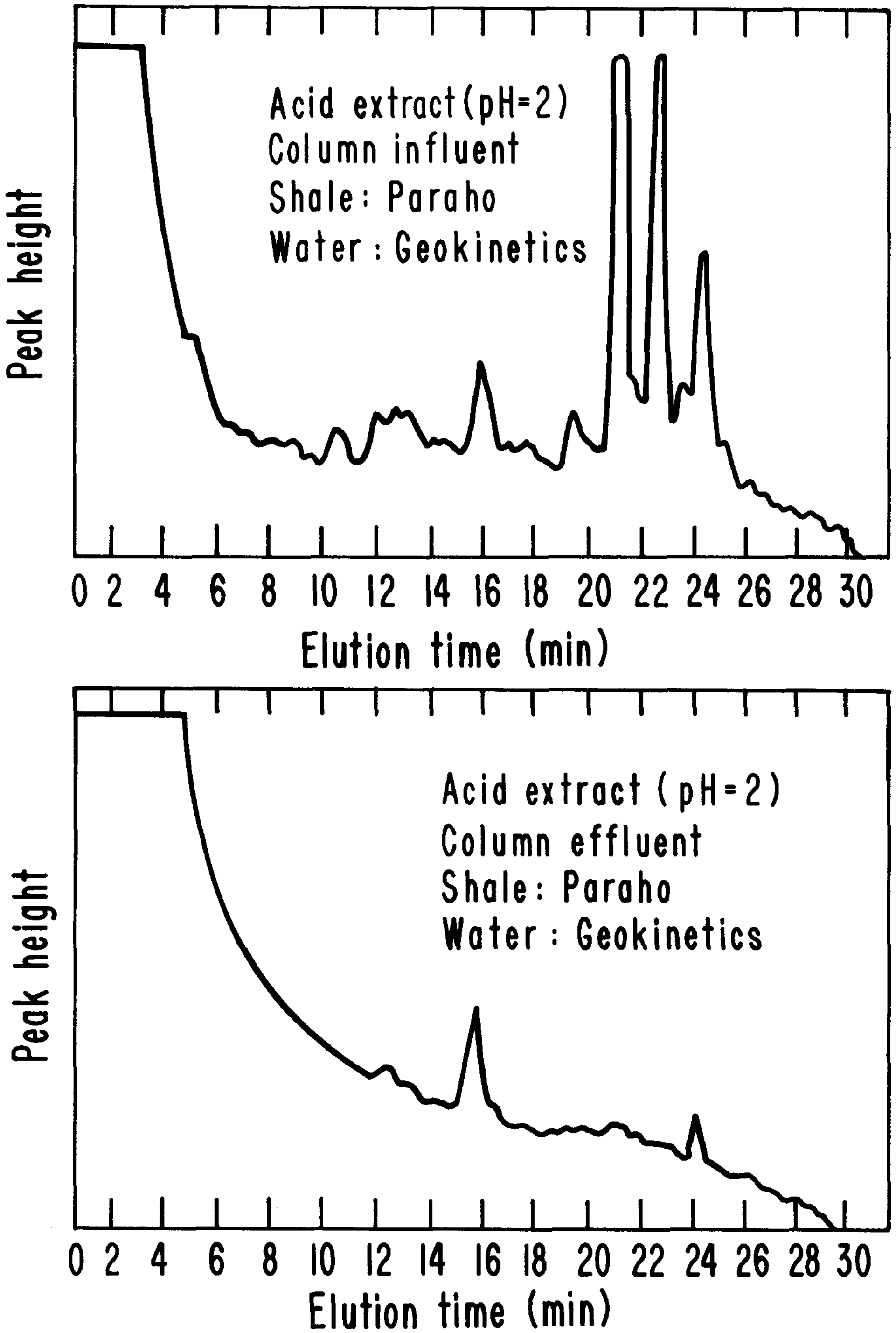

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Figure 18. Gas chromatography fingerprints of acid extracts of Paraho/ Geokinetics column influence and effluent.

indicate that spent shale may be used to reduce the organic and inorganic carbon, electrical conductivity, color, and odor and to elevate the pH of process waters. These characteristics have important and immediate applications to the treatment of retort water. A conventional system to treat retort water is shown in Figure 19a. Oil and grease removal would be followed by steam stripping to remove NH_3, biological treatment to reduce soluble organics, and a desalination step to remove dissolved salts. The results of this work suggest that a system similar to that shown in Figure 19b is feasible. A packed bed of spent shale could be placed ahead of the ammonia removal step. The increase in pH achieved in the spent shale column would convert NH_4 to NH_3 which could be readily removed from the water by air stripping instead of steam stripping. This would result in a cost saving because air stripping may be cheaper than steam stripping due to reduced energy requirements. The simultaneous reduction of conductivity and organic and inorganic carbon through the spent shale column would decrease the load of these constitutents on subsequent treatment steps, allowing the use of smaller units. It is possible that spent shale treatment may remove toxic organic components. This would improve the operation of the biological treatment system. These features of using spent shale columns could result in considerable cost savings over conventional treatment systems.

Based on these results, work was initiated to prepare the treatment system shown in Figure 19b. Treatability studies were started on oil and grease removal, ammonia stripping, and biological

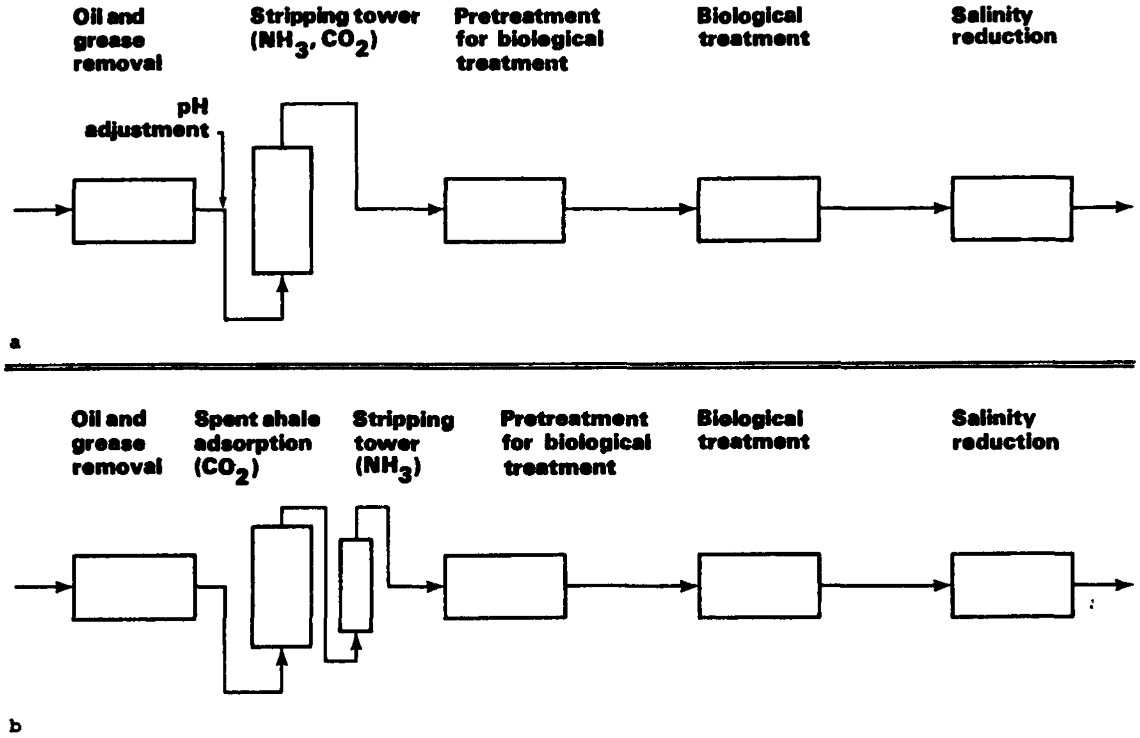

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Figure 19. Proposed treatment system for upgrading retort water: (a) using conventional technology; (b) using columns of spent shale.

oxidation. The following sections summarize the results of the oil and grease removal and the ammonia stripping work. The biological studies are in progress, but it is too early at this point to report results.

Oil and Grease Removal

It was initially assumed that retort waters contained a significant fraction of emulsified oil and grease. This widely held opinion among oil shale researchers was based on information concerning the production of retort water and on experimental measurements. Fox (1979) noted that filtration of retort water through 0.45 m filter paper deposited a matte of apparently oily materials that had an odor and appearance characteristic of shale oil. Visual observation of retort waters stored in polyethylene containers on this program indicated that an oily layer was deposited on the walls of the containers. Other investigators measured oil and grease levels in retort waters of 3800 mg/l (Fox et al., 1978; Harding et al., 1978). These observations and measurements were consistent with the production of retort water, which is generated within the retort system as a vapor that is condensed out with the oil. The oil and water are separated by heating and decantation, and some of the oil may remain associated with the water phase.

Since emulsified oil and grease can interfere with treatment processes by coating an adsorption medium such as spent shale, studies were initiated to develop methods to remove the oil and grease from the waters before spent shale treatment. Because we believed that there were high concentrations of suspended oil and grease in these waters, we selected coagulation followed by dissolved air flotation, the method conventionally used to treat refinery effluents because it allows reclamation of the oil.

However, in the course of this work, we discovered that only a small fraction of the "measured" oil and grease in retort water consists of mineral hydrocarbons, i.e., oil and grease, and that this fraction is emulsified. The balance of the "measured" oil and grease is dissolved organic material, which is extracted during the standard oil and grease test, and polar high-molecular-weight materials. This additional material probably includes large quantities of carboxylic acids and heavy ends such as asphaltenes. This discovery brought a decision to develop a reliable oil and grease test (see p. 36). Work is now in progress to characterize this dissolved material to determine whether or not it should be removed from oil shale process waters.

This section reports the results of experimental work to select a suitable coagulant for oil and grease in retort waters. Zeta potentials of retort waters were measured and screened, and jar tests were performed on several chemical coagulants and polymers and two retort waters. This work indicated that the surface charge of the suspended particles in retort water is negative and that several cationic polymers produce particle aggregates ("floc") at dosages in excess of 100 ppm. Oil and grease removal even at these high dosages was poor. These results are partially attributed to the fact that only a fraction of the oil and grease is particulate and therefore amenable to coagulation. Because of the low oil and grease removals and high dosages of polymer, we do not believe that coagulation will effectively remove oil and grease from retort waters.

Coagulation and Flocculation. Large particles in a wastewater are conventionally removed by gravity sedimentation. However, very small particles and colloids are too small to be removed in this way because of their very slow settling velocities. These much smaller particles are removed from a water by first coalescing them into larger particles and then using conventional removal mechanisms, such as sedimentation or flotation, to remove these newly formed larger particles. Coagulation refers to particle aggregation, or the process of making large particles out of small ones; flocculation refers to the transport of the aggregated particles. The aggregated particles are referred to as "floc."

Colloidal particles remain in suspension due to the high surface charge that they carry. These surface charges develop by preferential adsorption, ionization, and isomorphous replacement. Oil droplets tend to acquire a negative charge by preferential adsorption of anions, particularly hydroxyl ions. This surface charge must be reduced to accomplish particle aggregation or coagulation by the addition of electrolytes, polymers, or chemicals that form hydrolyzed metal ions, such as alum and ferric sulfate. The mechanisms responsible for coagulation using these types of substances are discussed elsewhere (Weber, 1972).

Zeta Potential. Zeta potential measurements are commonly used to estimate the surface potential of suspended particles. The measurement can be used to assess the type and doses of a coagulant required for floc formation. Zeta potential, ζ, is defined by the equation

$$\zeta = 4\pi\delta q/D$$

where q = the charge on the particle (or the charge difference between the particle and the body of the solution)

δ = the thickness of the layer around the particle through which the charge difference is effective

D = the dielectric constant of the solution.

Thus, the zeta potential is a measure of both the charge on the colloidal particle and the distance over which the charge is effective.

Zeta potential is determined by measuring the velocity of a particle in an electrical field. The velocity is directly proportional to the zeta potential, applied field strentgth, and solution dielectric constant, and is inversely proportional to the solution viscosity.

High specific conductance, a characteristic of retort water, complicates the measurement of zeta potential. These problems include: 1) thermal overturn, caused by ionic friction and resulting in the particles deviating from a straight path, 2) slow velocities caused by the low applied voltage, which causes problems in particle velocity measurements and possible settling of the particles within the cell, and 3) "salting out" which lowers the zeta potential of the particle.

The problem of high specific conductance was reduced by diluting the sample. (The zeta potential curve in Figure 20 for L-3 retort water was obtained in this manner.)

Zeta potential analysis demonstrated a decrease in the negative mobility of the particles with decreasing dilutions caused the influx of positive counter ions into the diffuse double layer of charge around the droplets. A plateau of negative mobility at approximately -1.35 μm/sec per volt/cm was attained at a dilution of about 20 percent (v/v). The zeta potential of the particles in L-3 retort water was about -1.35 μm/sec per volt/cm.

The negative charge on the droplets indicates that they can be coagulated with a cationic polymer or a metal salt. On the other hand, the high ionic strength of the retort waters tends to suppress the diffuse double layer around the oil droplets. This should enhance coagulation. However, the high ionic strength also tends to inhibit the coagulative potential of the polymers. The net result is generally an increase in the dose of coagulant required to achieve good flocculation.

<u>Coagulant Performance by Jar Testing</u>. A variety of metal salts and polymers was first visually screened for floc formation using L-2 retort water. The more successful of these were then evaluated using standard jar testing methods and L-2 and 150-ton retort waters.

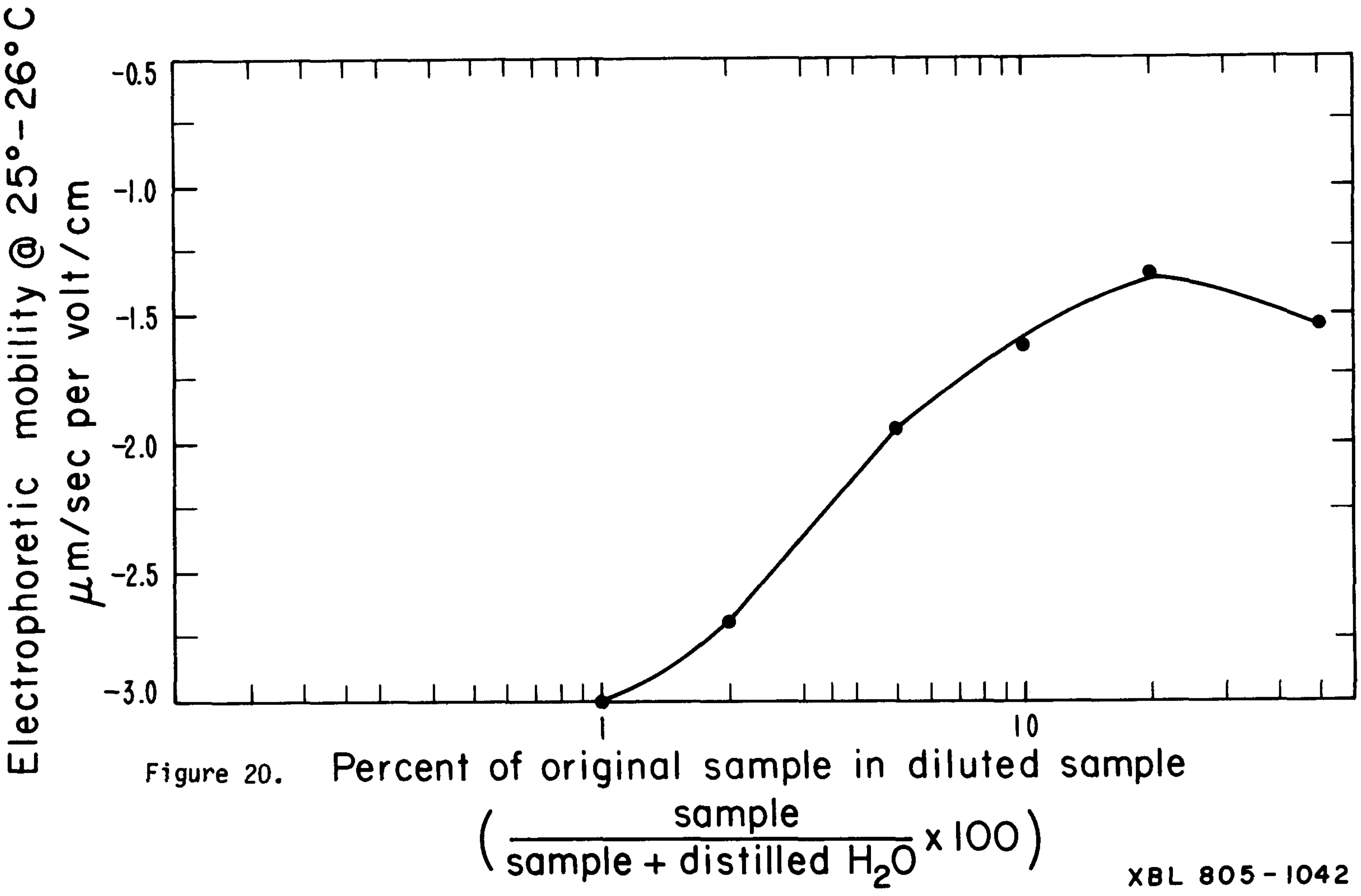

Figure 20.

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Coagulant performance was evaluated by measuring residual turbidity because Luthy (1976) demonstrated a positive correlation between residual emulsified oil and turbidity. Only results for L-3 water are presented here because the SMCE of the 150-ton water was below the detection limit of the analytical method used.

In the screening tests, alum, ferric chloride ($FeCl_3$), ferric sulfate [$Fe(SO_4)_3$], and a total of 36 commercial anionic, non-ionic, and cationic polymers were tested for their ability to produce a visible floc. This was accomplished by taking a 50 ml sample of retort water and dosing it with a given concentration of polymer. The sample was then stirred for 30 seconds with a magnetic stirrer and checked for visible signs of floc formation. Table 12 summarizes the results of these screening tests. This table indicates that the most successful polymers were Tretolite and Nalco. Many of the polymers, particularly Tretolite, produced non-settleable flocs.

The second screening procedure involved dosing a 50-ml sample of retort water with a known concentration of polymer. After 30 seconds of rapid stirring, the sample was allowed to settle for 60 minutes. An aliquot of the supernatant was drawn off and residual turbidity was measured. This procedure was repeated for a range of polymer doses to determine the dose that produced minimum residual turbidity in the wastewater, the value commonly referred to as the optimum coagulant dose. The results of the jar tests for the six most promising coagulants, in terms of turbidity removal, are shown in Figures 21 and 22. Table 13 lists the optimum coagulant dose and corresponding

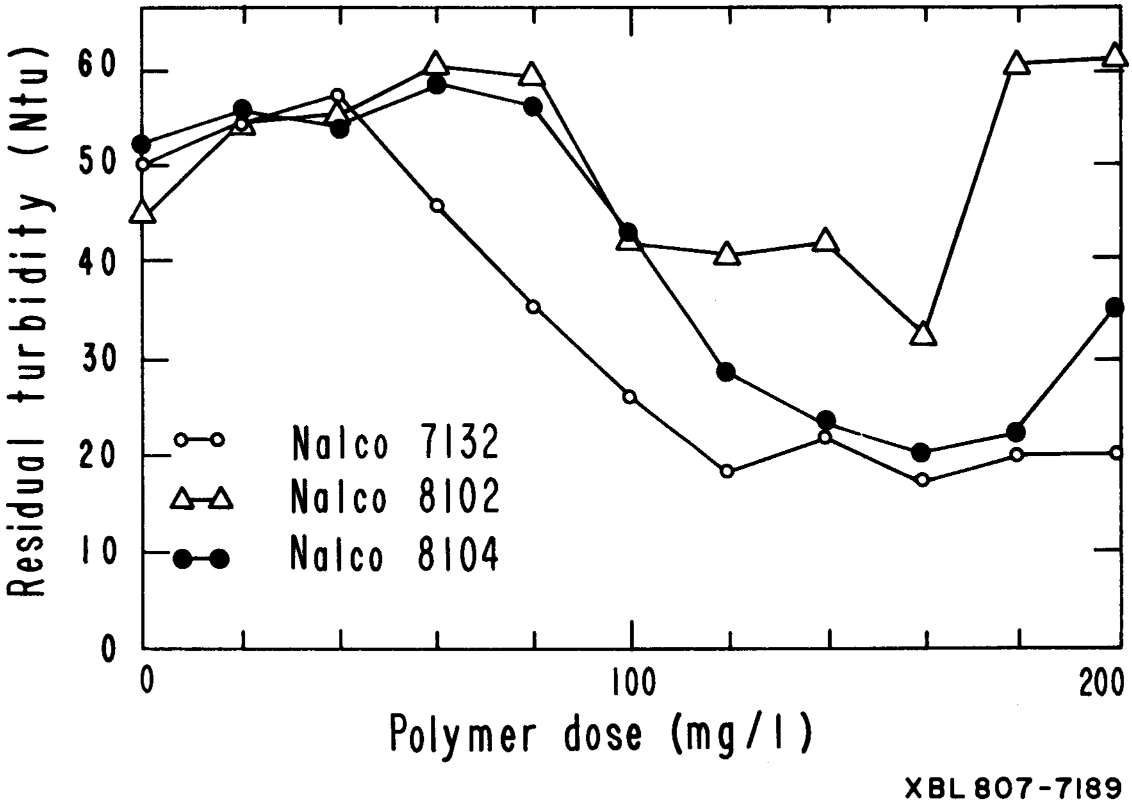

Figure 21. Effect of Nalco 7132, 8102, and 8104 on the residual torbidity of L-3 retort water.

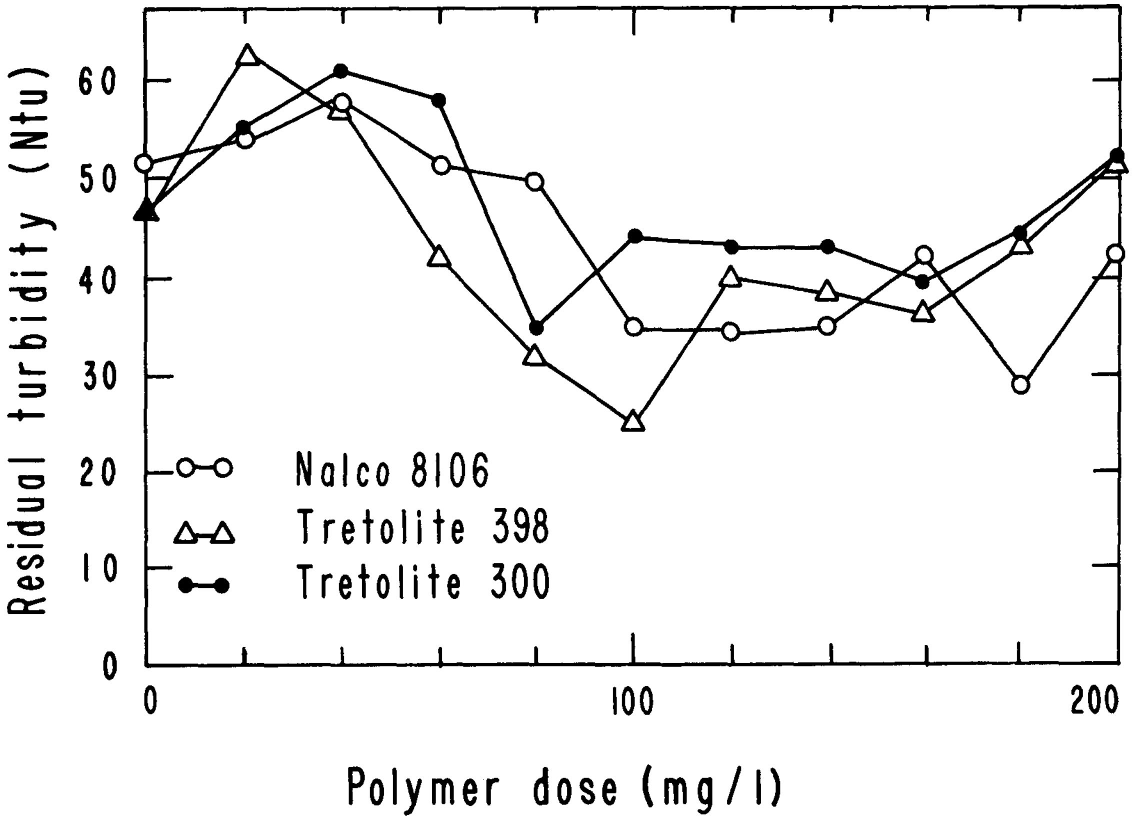

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Figure 22. Effect of Nalco 8106 and Tretolite 300 and 398 on the residual torbidity of L-3 retort water.

Table 12. Summary of screening test of various coagulant aids using L-2 retort water.

Name of Polsmer	Chemical Make Up Description	Floc Formation +/-
American Cyanamid		
Magnifloc		
1561C		-
1839A		-
1906N		-
521CH	Polyamide	-
581C		-
507C		+
587C		-
Tretolite		
J-189		+
TFL-300	Quaternary	+
TFL-362		+
TFL-383		+
TFL-391	Polyamires	+
TFL-398	Polyamine	+
Calgon		
WT 3000		
CAT FLOC	Pdadma	+
WT 2575	Pdadma	-
WT 2640	Pdadma	
Carret-Callahan		
LDOW		
766N		
764N		+
720 CL	Polyamine (Dark Amber)	-
721 CL		
Herco Floc 863 (Dry)		-
Nalco		
603		-
7103		+
7105		+
7107		+
7132		+
7134		+
7123		+
7730		+
7731		+
7734		-
8101		+
8102		+
8104		+
8106		+
Alum		+
$FeCl_3$		+
$Fe_2(SO_4)_3$		+

turbidity reduction for Nalco and Tretolite polymers and L-3 and 150-ton retort waters. All of these polymers, except Tretolite 398, were found inadequate with 150-ton retort water, presumably due to low concentrations of suspended solids. The residual turbidity following coagulation and settling either remained constant or increased. All of the successful polymers were cationic, which is consistent with the zeta potential measurements reported previously. Table 13 indicates that polymer doses of 40 to 160 ppm were required to effect turbidity reductions of 12 to 64 percent. These results are not encouraging because of the high dosages required.

The trends in Figures 21 and 22 are typical for turbidity removal by coagulation and flocculation with polymers and metal salts. Constant or slightly increasing residual turbidity indicates Zone I flocculation, in which the coagulant dose is insufficient to obtain good turbidity removal. The residual turbidity decreases in Zone II as floc formation occurs. The optimum coagulant dose occurs in Zone II at the point where the turbidity reaches a minimum. In Zone III a charge reversal occurs and the particles are resuspended, which increases the turbidity.

Based on the results presented in Table 13, additional coagulation tests were performed with 150-ton retort water and Tretolite 398 polymer. This combination was evaluated in a series of jar tests employing oil and grease removal, rather than residual turbidity, as a means of evaluating process performance.

Table 13. The effect of Tretolite and Nalco polymers on residual turbidity of two oil shale retort waters.

Coagulant	Retort Water	Dosage[a]	Turbidity eduction
Nalco 7132	L-3	120	64
Nalco 8102	L-3	160	29
Nalco 8104	L-3	160	62
Nalco 8106	L-3	100	49
Tretolite 398	L-3	100	47
Tretolite 300	L-3	80	28
Nalco 7132	150-ton	---	Increased Turb.
Nalco 8102	150-ton	---	Increased Turb.
Naclo 8106	150-ton	---	Increased Turb.
Tretolite 398	150-ton	40	12
Tretolite 300	150-ton	---	Increased Turb.

[a] Dosage required to produce minimum turbidity following jar testing.

Varying doses of Tretolite 398 were added to jars containing 250 ml of 150-ton retort water. The samples were rapidly mixed at 150 rpm with a standard jar test apparatus for 60 seconds. This was followed by slow stirring for 15 minutes at 40 rpm. The samples were then centrifuged for 15 minutes at 2500 rpm. Portions of the supernatant were withdrawn from beneath the liquid surface and analyzed for oil and grease (SMCE) by methods previously discussed. The results, summarized in Figure 23, show total and suspended oil and grease as a function of polymer dose. The polymer was not effective at removing the SMCE fraction.

The pertinent conclusions from this work are as follows:

- The suspended portion of oil and grease in the various retort waters is relatively small and is not sufficient to warrant removal for commercial or process reasons.
- Polymer dosages required to effect reduction in turbidity are large, 40 to 160 ppm, and the percent turbidity reduction relatively small, 12 to 64 percent. These results suggest that coagulation and dissolved air flotation would not be suitable for achieving low effluent oil and grease concentrations and that this process would not be economic because of the high polymer dosages.
- The analytical method used to measure oil and grease is inadequate. Additional work is required to develop and refine accurate methods to measure oil and grease and to characterize the suspended material in oil shale process waters.

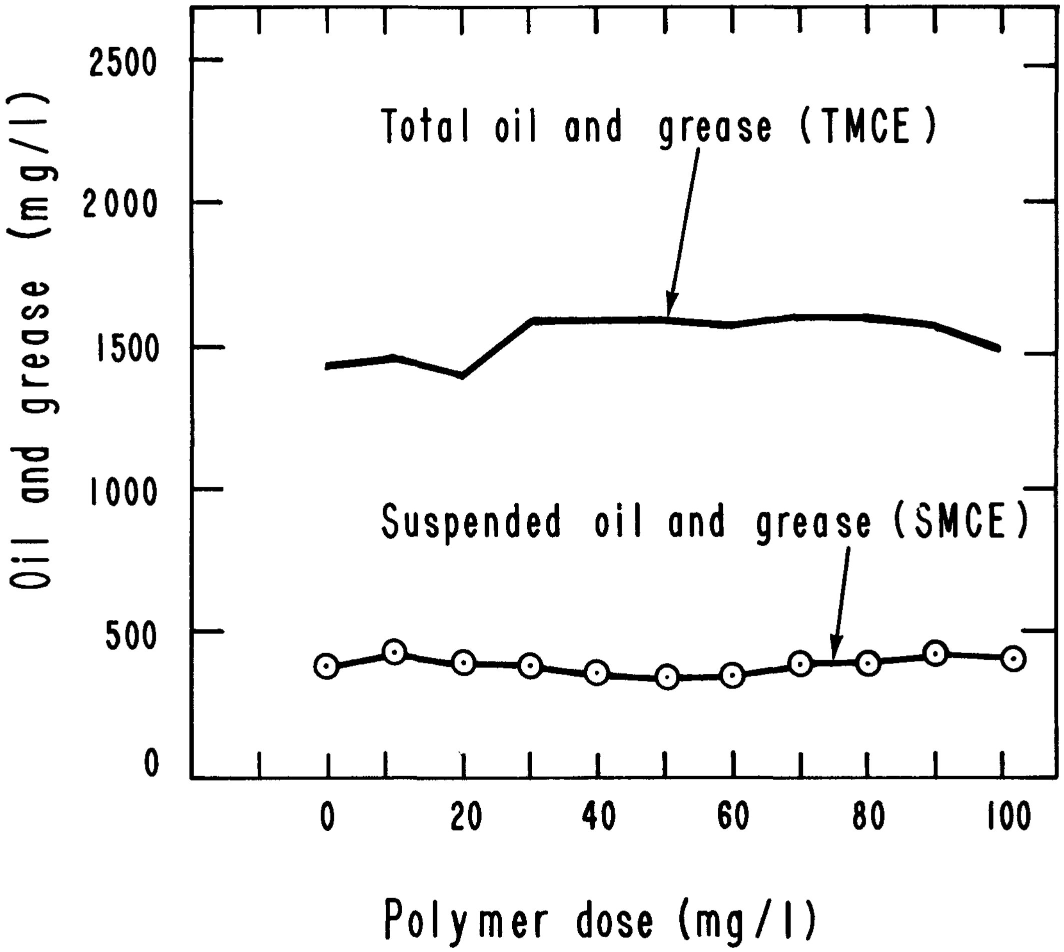

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Figure 23. Effect of Tretolite 398 on the total and suspended oil and grease content of 150-ton retort water.

Therefore, coagulant tests were discontinued and research emphasis shifted to the development of a reliable oil and grease analytical method. When such a test is available, it will be used to characterize the oil and grease and other suspended material in several process waters. Based on this characterization data, treatment processes suitable to reduce the suspended material will be selected and tested in laboratory studies.

Ammonia Stripping

Retort waters and gas condensates contain elevated concentrations of ammonia (NH_3) which will have to be removed from the water before it can be treated in downstream treatment units, re-used on site, or discharged. Ammonia nitrogen concentrations in excess of 4,000 mg/l are toxic to biologic oxidation processes. Ammonia is also toxic to aquatic biota, particularly fish, if the waters are discharged; and it must be removed before a water can be used as makeup for a boiler or cooling tower.

Preliminary batch studies were initiated to assess air versus steam stripping of NH_3 from retort waters and to prepare large volumes of ammonia-stripped water for use in activated sludge studies.

Experimental. Batch studies were conducted to evaluate ammonia stripping from 150-ton retort water. A measured quantity of retort water at room temperature was placed in a 2-liter graduated breaker, the pH was adjusted to 12.9 - 13.0 with a 50 percent sodium hydroxide (NaOH) solution, and the sample was aerated at various flow rates and times using an air stone. The change in ammonia concentration with time was measured by the titrimetric method outlined in Standard Methods (1976). Volatile acids were measured to investigate foaming problems that occurred during aeration. The steam distillation method in Standard Methods (1976) was used for volatile acids.

Results and Discussion. Ammonia (NH_3) may be removed from retort waters by elevating the pH and stripping out the NH_3 at ambient temperatures or by elevating the water temperature and stripping out the NH_3 at the sample pH or a slightly higher pH. In the first case, the pH must be elevated to convert ammonium ion (NH_4) to ammonia gas (NH_3). At the sample pH of 150-ton retort water (8.7), only about 33 percent of the NH_3 is in gaseous form and stripping at ambient temperature is not efficient. (At a pH of 12.5, essentially all of the NH_3 is in the gaseous form, and is thus more readily stripped.) Figure 24 indicates that at a constant air flow of 4.25 scfh (at pH 8.7), only 22 percent of the NH_3 was removed in 11 hours.

Figure 24 indicates that ammonia stripping is also enhanced at higher flow rates. However, excessive foaming of the retort water occurred during aeration and liquid was lost over the side of the basin. Foaming decreased at lower flow rates. It may be feasible to beneficially use foam production in retort water treatment. Foam fractionation may be suitable for removing suspended oil and grease and to reduce the concentration of surface active agents. Volatile acids decreased 31 to 40 percent (Table 14), during aeration. This will be investigated in future work.

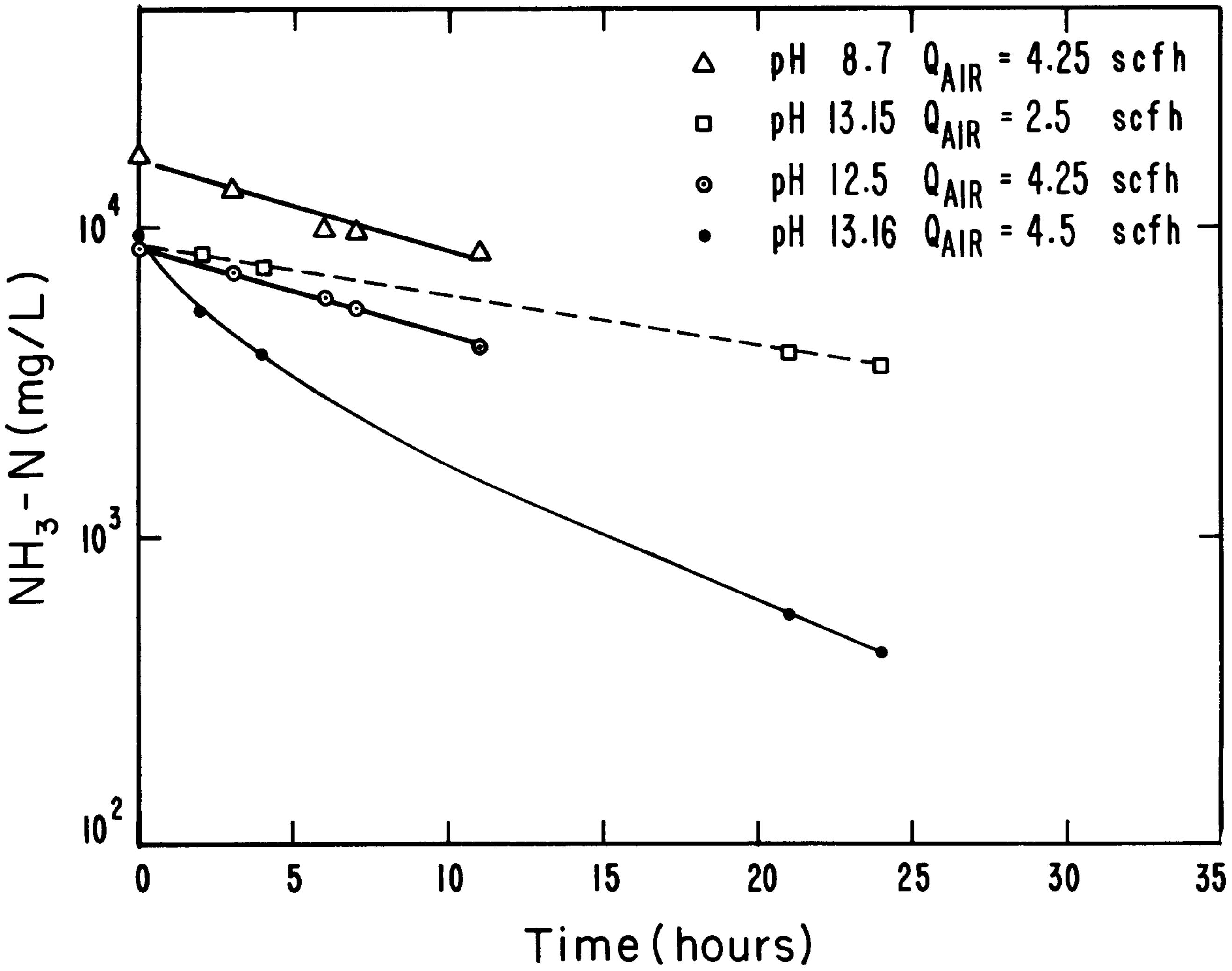

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Figure 24. Reduction of ammonia by batch aeration demonstrating the effect of pH and airflow on the ammonia removal process.

Table 14. Reduction of volatile acids in 150-ton retort water by foam fractionation.

Air Flow, schf	Volatile acids ppm as acetic acid 150-ton retort water	Aeration time, Hours	pH	Volatile acids, ppm as acetic acid	Volatile acid reduction
4.25	5128	11	12.5	3060	40
4.25	5128	11	8.7	3551	31

Ammonia may also be removed by steam stripping. The Henry's Law constant increases exponentially with water temperature and the equilibrium between NH_4 and NH_3 shifts in favor of NH_3 at higher temperatures. Both of these factors enhance the stripping of ammonia. This will be investigated in future studies.

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