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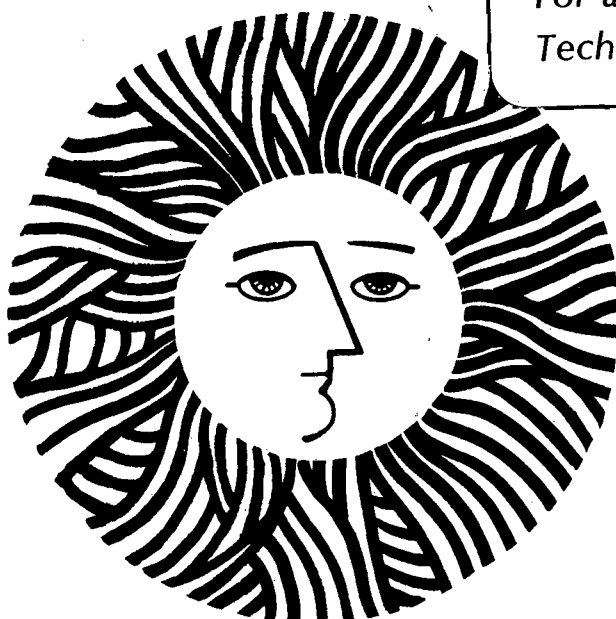## UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

PHYSICOCHEMICAL TREATMENT METHODS FOR OIL SHALE
WASTEWATER: EVALUATION AS AIDS TO BIOOXIDATION

B.M. Jones, R.H. Sakaji, and C.G. Daughton

July 1982

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Physicochemical Treatment Methods for Oil Shale Wastewater:

Evaluation as Aids to Biooxidation

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PHYSICOCHEMICAL TREATMENT METHODS FOR OIL SHALE WASTEWATER: EVALUATION AS AIDS TO BIOOXIDATION

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ABSTRACT

Biological treatment is usually effective for the mineralization of only one half of the organic carbon present in retort waters. Microbial growth is supported primarily by polar organic constituents, especially fatty acids. Explanations for the limitation to biooxidation are proposed, and several physicochemical treatment methods including sorption and chemical oxidation were evaluated for their abilities to complement or enhance biooxidation.

The use of spent shale or powdered activated carbon (PAC) effected preferential sorption of the less polar, biorefractory organic compounds from retort water. The concurrent application of these sorbents with biooxidation, however, did not promote a synergistic removal. The construction and application of a "pilot-scale" adiabatic stainless steel and beaded-glass steam stripper for removal of ammonia, hydrogen sulfide, and carbon dioxide from oil shale process wastewaters is discussed; emphasis is placed on the benefits steam stripping would accord biooxidation. Ultraviolet radiation had no significant effect on the biorefractory organic solutes in retort water. Extensive ozonation structurally altered 14 percent of the recalcitrant dissolved organic carbon (DOC) and thereby promoted enhanced microbial mineralization. Ozonation mediated by ultraviolet radiation had a synergistic effect. More than 41 percent of the DOC, however, remained refractory to successive treatments by primary biooxidation, exhaustive chemical oxidation, and secondary biotreatment. Potent chemical oxidants apparently were incapable of effecting sufficient structural alteration of the biorefractory compounds to encourage renewed biooxidation. This implies that

oxidative enzyme systems also may be incapable of promoting further alteration or mineralization of these recalcitrant solutes. Physicochemical methods that complement biotreatment may be required to upgrade oil shale wastewaters for reuse or codisposal.

INTRODUCTION

Successful treatment of oil shale wastewater will undoubtedly require the application of more than one method. A particular method may be extremely effective for the removal of specific classes of organic compounds, but, when applied to a heterogeneous mixture such as retort water, it may be able to remove only a fraction of the contaminative solutes. Extensive treatment of these waters will require a combination of methods that yield complementary or enhanced performance when used in sequential or simultaneous applications. The integrated processes should be evaluated carefully because the final degree of treatment can be additive (i.e., the sum of the individual processes), synergistic (i.e., greater than the sum of the processes), antagonistic (e.g., lower than any of the processes), or combinations thereof.

The success of biological wastewater treatment totally depends on the ability of an acclimated microbial community to mineralize the organic contaminants. Microbial growth in Oxy-6 retort water is eventually limited by bioavailable carbon (Jones et al., 1982). Approximately 50 percent of the organic carbon is amenable to biooxidation; the remaining organic compounds are recalcitrant. These refractory compounds are predominantly nonpolar solutes such as nitrogen and oxygen heterocycles and aromatic amines (Jones et al., 1982).

In the work reported here, three physico-chemical treatment methods were assessed as aids to biooxidation of organic solutes in oil shale process wastewater. (i) The removal of DOC by spent shale or powdered activated carbon (PAC) sorption in sequential and simultaneous configuration with biological treatment was evaluated. (ii) The potential applicability of steam stripping for enhancement of microbial mineralization was reviewed; a pilot-scale unit was designed and constructed. (iii) The mineralization and structural alteration of biorefractory compounds by ultraviolet (UV) irradiation and ozonation was investigated.

Complementary treatment performance can be achieved merely by the physical removal of biorefractory compounds. Treatment methods that selectively remove organic constituents associated with the nonpolar, lipophilic fraction (LpF) (Daughton, Jones, and Sakaji, 1982) of the dissolved organic carbon (DOC) would effect an additive degree of treatment when integrated with biooxidation. Sorbents such as spent shale or PAC were evaluated for this purpose.

Enhancement of biotreatment can be attained by the removal of constituents that prevent the catabolism of other solutes because of toxicity or repression of catabolic enzyme systems. The presence of easily utilizable ammonia-nitrogen in oil shale wastewaters can result either in the repression of those enzyme systems that are capable of extracting the ring-bound nitrogen of heterocyclic compounds (Cook and Hütter, 1981; Jones et al., 1982; Watson and Cain, 1975) or in the inhibition of biological oxidation. The removal of ammonia by steam stripping would minimize these effects.

Two other major factors that exacerbate the refractory nature of the heterocycles in retort water are (i) the presence of numerous homologs and variants, each of which often requires a specialized catabolic enzyme system, and (ii) the low individual heterocycle concentrations, which are sufficiently below the affinity or threshold values for the requisite enzymes (Daughton, 1981). The second factor could be negated by increasing the apparent concentrations of both the diluted solutes and the bacterial cells. Both spent shale

and PAC provide a sorptive surface that can increase the relative concentration of solutes; they were added to bacterial suspensions and evaluated for their ability to enhance biooxidation.

Ozonation and UV irradiation can possibly augment or enhance biological treatment by mineralization or oxidative alteration of recalcitrant organic solutes and toxicants in oil shale wastewaters. These two processes could also hinder biooxidation by (i) producing toxicants, (ii) polymerizing solutes that would ordinarily be biodegradable, or (iii) amplifying the existing problem of a multitude of solutes each present at low concentration. The effects of ozonation and UV irradiation may also model the maximum capacity of aerobic biooxidation (Jones et al., May 1982) and the effects of ponding these waters at the relatively high elevations of the western oil shale regions prior to treatment, reuse, or codisposal.

BACKGROUND

Microbial growth in Oxy-6 retort water is initially limited by inorganic orthophosphate (Jones et al., 1982). Paradoxically, the ensuing limiting nutrient becomes carbon, even though repeated studies have shown that about one half of the DOC remains after exhaustive biological treatment (Hicks et al., 1980; Jones et al., 1982). The addition of other trace elements does not elicit an increase in growth or DOC removal. Further growth is observed, however, when these same cultures are supplemented with an exogenous source of easily degraded carbon, such as fatty acids (Jones et al., 1982). Nitrogen and oxygen heterocycles and aromatic amines have been strongly implicated (Daughton et al., unpublished data) as the major chemical classes responsible for the extraordinary recalcitrance of organic carbon in the extracellular fluid that remains after exhaustive biooxidation of retort water (i.e., spent retort water). This hypothesis has been strengthened by several reports on chemical characterization of Oxy-6 retort water extracts (e.g., Raphaelian and Harrison, 1981) that indicate the presence of numerous aromatic amines and nitrogen heterocycles at low part-per-million concentrations.

Even if the carbon that remains after extensive biological treatment were not inherently recalcitrant, the following points (Daughton, unpublished observations) may explain the paradox and illustrate the reasons for evaluating the physicochemical methods reported here. (i) A large portion of the recalcitrant carbon is composed of nitrogen heterocycles and aromatic amines. (ii) Substituted nitrogen heterocycles, especially pyridines, are not necessarily resistant to microbial metabolism, but the requisite enzymes are apparently highly substrate specific. This would perhaps necessitate the use of many acclimated bacterial species. (iii) This carbon is shared among numerous isomers, homologs, and variants of organic nitrogen compounds; each compound may therefore be present at a concentration below the requisite enzyme affinity value. (iv) Enzyme induction often may occur only when nitrogen becomes a limiting nutrient.

Sorption

Spent shale is the solid waste by-product from the retorting of oil shale. Previous investigations have shown that spent shales from different retorting processes can effect the removal of DOC or dissolved inorganic carbon (DIC) from retort water (Fox, Jackson, and Sakaji, 1980; Sakaji, Jones, and Daughton, 1981). The ability of spent shales to act as sorbents is apparently dependent on the conditions that the surface of the shale has experienced during retorting. Spent shales that result from low-temperature retorting, such as the TOSCO II process, retain a residual char on the surface and are effective for the sorption of organic compounds (Fox et al., 1980). The char is purported to act in a manner analogous to activated carbon for the adsorption of solutes.

Wastewaters from a spectrum of industries have been upgraded by contact with activated carbon. Activated carbon is effective for adsorbing organic solutes, especially those which impart color and odor, from petroleum refinery sour waters. In addition to sequential treatment, PAC has been used in simultaneous application with biooxidation to supposedly promote enhanced contaminant removal.

The feasibility of using either TOSCO II spent shale or PAC as sole agents for upgrading Oxy-6 retort water has been assessed (Sakaji et al.,

1982). Fitting the data to the Freundlich equation ($q_e = mC_e^{1/n}$) revealed that neither spent shale nor PAC would be considered a favorable sorbent for retort water solutes. These results can be partially attributed to the nonspecificity of DOC as a measurement of solute concentrations. Although spent shale and PAC are not the panacea for retort water treatment, the possibility that they may preferentially sorb nonbiodegradable compounds motivated the present studies.

Steam Stripper

Steam stripping is commonly used by the petroleum industry for the removal of carbon dioxide, hydrogen sulfide, and ammonia from refinery wastewaters. Ammonia can be effectively removed by steam stripping because of the concomitant reduction of the pK_a of the ammonium ion-ammonia gas equilibrium and the solubility of ammonia gas at elevated temperatures. The stripping of these compounds by steam involves: (i) the conversion of ionic species, such as ammonium, bicarbonate, and carbonate, into their neutral, gaseous forms, i.e., ammonia and carbon dioxide, (ii) the diffusion of the dissolved gases from the bulk solution to the liquid-steam interface, and (iii) the transfer of the dissolved gas through the liquid-steam interface into the steam phase.

The complex interactions between dissolved species in oil shale wastewaters complicate this idealized model for steam stripping. Species such as hydrogen sulfide and organic acids can pair with the ammonium ion (Bomberger and Smith, 1977), thereby decreasing the partial pressure of ammonia in the gas phase and the propensity of the gas to be removed from the liquid phase.

The stripping of ammonia from oil shale wastewater has been evaluated by several investigators. Murphy, Hines, and Poulson (1978) report that hot air (93.2 $^\circ$C) saturated with water removes up to 99.5 percent of the ammonia and carbon dioxide from Omega-9 retort water. Habenicht et al. (1980) report ammonia and carbon dioxide removals from 150-Ton retort water of 54 and 57 percent, respectively, by steam stripping. The batch stripping of heated Oxy-6 gas condensate achieves 98 percent removal of ammonia (Hicks et al., 1980). In a preliminary steam stripping

study, ammonia and carbon dioxide removal from Oxy-6 gas condensate is reported greater than 90 percent (Pearson et al., 1981). The pilot-scale steam stripper described in this report will be evaluated both as a pretreatment for biooxidation of oil shale wastewaters and as a polishing step prior to reuse of these waters.

UV Irradiation and Ozonation

Preliminary experiments using short sequential or combined exposures to low dosages of UV radiation and ozone were designed to model possible effects of environmental dosages of UV radiation on retort water and to evaluate economical dosages of either treatment method for use in conjunction with biological treatment. Low dosages of UV radiation or ozone for short exposure intervals were insufficient to either mineralize or alter the biorecalcitrant solutes in retort water (Jones et al., May 1982).

Prolonged exposure to the chemical and photochemical effects of UV irradiation and ozonation were conducted to demonstrate the extremely refractory nature of the organic solutes in spent retort water and to predict the maximum potential for microbial oxidation of the biorefractory organic solutes that could possibly be realized by the appropriate bacteria with competent enzyme complements. An extensive discussion of the background and results of this work has been completed (Jones et al., May 1982).

MATERIALS, METHODS, and EXPERIMENTAL DESIGN

Materials

Oil shale wastewater from the pilot-scale modified in-situ (MIS) retort burn #6 (Oxy-6; Occidental Oil Shale, Inc., Logan Wash, CO) was used in all experimental work. Samples of this water were collected from the oil-water separator (sample point #2) (Farrier, 1979), composited (Daughton and Sakaji, 1980), and distributed for interlaboratory comparison studies. In experiments that used "raw" Oxy-6 retort water, the wastewater was not pretreated. "Spent" retort water, the extracellular fluid that remains after exhaustive biooxidation, was generated in 3-L batch cultures (raw retort water) that were aerated (2.5 L/min), mixed (500 rpm), and maintained at 30 °C in a Pyrex fermentor (model MA-107, New Brunswick

Scienific Co., Inc., Edison, NJ). These cultures were supplemented with 5.0 mL of concentrated phosphoric acid (final concentration 26 mM) and were inoculated with a highly acclimated microbial seed derived from soil, sewage, and industrial sources. At stationary phase (cessation of microbial growth, at 48 h), the microbial cells were separated from the extracellular fluid by centrifugation (13,300 x g at 4 °C for 30 min) followed by filtration of the supernatant fluid through 0.8-μm pore diameter polycarbonate membranes.

Spent shale, obtained from the TOSCO II surface retorting process (Colony Project, Parachute, CO), was graded (60-80 mesh for batch studies and 25-120 mesh for the continuous-flow column study) using a Ro-Tap sieve shaker. This spent shale had been retorted at 500 °C and had a surface area of 10.2 m^2/g (Fox et al., 1980). The PAC (12-40 mesh) had a surface area of 500 m^2/g (I.C.I. Americas, Inc., Wilmington, DE).

A 450-W, medium-pressure, full-emission mercury-arc lamp enclosed in a water-cooled quartz immersion well was used to generate ultraviolet light for the photooxidation investigations. The immersion well was placed directly in contact with approximately 900 mL of wastewater which was held in a photoreactor (model #7840-185, Ace Glass, Inc., Vineland, NJ) and stirred with a magnetic bar. The design of the apparatus permitted 40 to 50 percent of total volume to be in the reactive area. The photoreactor was also used as the reaction vessel for the ozonation and UV/ozonation experiments.

Ozone was produced by passing purified oxygen at a flow rate of 100 cm^3/min (STP) through an ozone generator (model 1-T, Aqueonics Division, ARCO Environmental, Inc., Dublin, CA). The ozone production rates were determined to be 6.36 and 6.53 mg/min for the ozonation and UV/ozonation experiments, respectively. Ozone was introduced to the wastewater through 1/16-in i.d. Teflon tubing at the bottom of the reactor directly above the magnetic stirrer.

Methods

Performance of treatment methods was estimated by quantitating organic carbon concentrations in filtrates from 0.4-μm pore diameter polycar-

bonate membranes (defined as dissolved organic carbon; DOC). High-temperature combustion (950 $^{\circ}$C) coupled with coulometric titration of the evolved CO_2 (Coulometrics, Inc., Wheat Ridge, CO) was used to determine the DOC values for the sorbent studies. For the photooxidation and ozonation investigations, a low-temperature UV-persulfate oxidation unit coupled with coulometric titration (Langlois et al, 1982) was used to quantitate DOC.

The separation of the polar and nonpolar organic solutes in retort water was accomplished by a miniaturized reverse-phase fractionation (RPF) chromatographic technique (Daughton et al., 1982). Polar organic solutes (the hydrophilic fraction; HpF) of the DOC pass through a reverse-phase cartridge and are collected with the aqueous effluent. Less-polar compounds (the lipophilic fraction; LpF) are retained by the packing material and can be subsequently eluted by methanol and, after evaporation of the methanol, reconstituted in ASTM Type I water for further investigations or analyses.

Ozone was measured using the starch/iodine method (Standard Methods..., 1981). Ozone from the generator and effluent (off-gas) from the batch reactor were sparged through a measured volume of 0.12 N potassium iodide solution. Ozone stoichiometrically oxidizes iodide to iodine. Ozone in the gas stream was determined from the volume of standardized thiosulfate solution required to titrate the iodine. Ozone consumed in the reactor was calculated by difference, assuming a constant rate of production by the generator.

To characterize the color removal effected by UV or ozone treatments, absorbance spectra from 200 to 850 nm were obtained in a 1-cm pathlength quartz cuvette with a Bausch & Lomb 2000 UV-vis scanning spectrophotometer.

Microbial biomass of experimental cultures was approximated by determining the intracellular protein concentration. The procedure involves cell harvest, cell digestion (i.e., protein liberation), and quantitation of whole cell protein by the Lowry assay (Yu et al, 1981).

Experimental Design

Biooxidation. To evaluate the effectiveness of a physicochemical treatment method to complement or enhance biological mineralization of organic solutes, either the method was applied simultaneously with biotreatment (combined sorbent-biotreatment experiment) or a pretreated sample was subjected to microbial oxidation. The retort water samples (15 mL) were diluted with 5.0 mL of 156 mM phosphate buffer, 9.5 mL of ASTM Type I water, and 5.0 mL of a trace nutrient solution (0.72 mM $FeSO_4 \cdot 7H_2O$ and 99.7 mM $MgSO_4 \cdot 7H_2O$). The culture media were inoculated with 100 µL of a microbial community that had been acclimated to 50-percent raw Oxy-6 retort water and then incubated in either 125- or 250-mL baffled Erlenmeyer flasks (Bellco Glass, Inc., Vineland, NJ) at 120 rpm and 30 $^{\circ}$C in a shaker bath (model G76; New Brunswick Scientific Co., Inc., Edison, NJ). For the ozonation experiments, any residual ozone was allowed to dissipate for 24 hours prior to inoculation. The flasks were stoppered with cotton to minimize evaporation while allowing oxygen transfer. The cultures were maintained for 48 to 72 hours or until stationary phase was confirmed by color-corrected nephelometry (HF Instruments Limited, Bolton, Ontario, Canada). Samples from the outgrown cultures were filtered through 0.4-µm pore diameter polycarbonate membranes (the samples from the combined sorbent-biotreatment experiment were centrifuged prior to filtration) and the filtrates were analyzed for DOC concentration.

Sorption. The feasibility of using sorbents as aids to biological removal of organic contaminants from retort water was investigated using three different experimental designs. (i) Sequential treatment; treated retort water effluent from a continuous-flow spent shale column served as sole carbon and nitrogen sources for microbial inocula. (ii) Distribution studies; the removals of carbon from different RPF fractions of retort water by sorption and biotreatment were compared. (iii) Simultaneous treatment; the combined effects of biotreatment and sorption by either spent shale or PAC were evaluated. The sorbent dosage and time required to achieve equilibrium for the batch experiments were determined from previous work with spent shale and activated carbon (Sakaji et al., 1982).

Continuous-flow column study. Retort water was applied in an upflow mode at a surface loading rate of 0.68 L/sec-m^2 with a peristaltic pump (model 375A, Sage Instruments Division, Orion Research Inc., Cambridge, MA) to TOSCO II spent shale held in a fixed-bed Plexiglas column (5.1-cm i.d. x 914 cm). Time-course samples of the column effluent were collected for DOC analyses and for biological oxidation experiments.

Distribution study. The polar and nonpolar solutes of retort water were separated by RPF. The aqueous effluent of the chromatographic cartridge, which contained the HpF, was used directly; the LpF was eluted, brought to dryness under nitrogen, and reconstituted with ASTM Type I water. To determine if spent shale preferentially sorbed the components from one fraction, 3 g of spent shale was added to replicate 4-mL samples of each retort water fraction. The fractions were sampled periodically over 48 hours, and the DOC concentration of the time-course samples was compared with the initial DOC. The ability of each of the two fractions of retort water organic solutes to support microbial growth was investigated in parallel experiments. Each fraction was inoculated, incubated, and sampled according to the procedure described above.

Combined sorbent-biotreatment study. Three dosages of spent shale (10, 100, and 500 mg/mL) or PAC (0.13, 1.3, and 6.6 mg/mL) were added to 30 mL of 50-percent, nutrient-supplemented raw retort water. These dosages were chosen to equalize the sorbent surface areas present in each parallel treatment. The sorbent-retort water mixtures were inoculated with acclimated bacteria and maintained at 30 $^\circ$C, as described previously. Biological control cultures consisted of retort water media without sorbent additions. The removal of DOC by the control culture was used as the estimate of biological mineralization of organic solutes in the experimental treatments, assuming the sorbents did not inhibit microbial growth. The decrease in DOC from each of the sorbent-dosed experimental flasks after 1 h of incubation was used as the estimate of removal by sorption alone. The cultures were maintained for 48 hours (presumptive stationary phase), and the DOC was determined. Enhancement, that is the

synergistic removal of organic solutes beyond that accounted for by sorption and biooxidation, was determined by subtracting the DOC removed by sorption and by biooxidation from the total DOC removed by the combined, simultaneous processes.

UV irradiation and ozonation. The effects of intensive UV irradiation and ozonation on the organic solutes in spent Oxy-6 retort water were examined in three experiments. A sample was exposed to either ozone or UV radiation for five hours or to the combined effects of the two treatments for six hours. The experiments were conducted at ambient temperature (23 $^\circ$C) and unaltered pH (9.7). During UV irradiation, the temperature increased to 28-30 $^\circ$C. Following extensive ozonation or UV/ozonation, the pH of the effluent declined to 8.6. At hourly intervals, 25-mL samples were withdrawn and filtered for DOC and absorbance measurements. From each time-course sample, 15 mL was used for evaluation of biotreatment by serving as the sole source of carbon and nitrogen.

RESULTS AND DISCUSSION
Sorption Studies

The feasibility of using sorbents to augment or enhance biooxidation was evaluated in both sequential and simultaneous configurations.

Continuous-flow column study. The efficacy of using spent shale as an aid to biooxidation was investigated by determining the biological mineralization of organic solutes that remained in shale-pretreated retort water. Of the raw retort water DOC, 43 percent was removed from the first pore-volume (233 mL) of effluent by the column of spent shale (540 g). Substantial color removal was also effected. Acclimated bacteria incubated in shake-flask cultures containing first-pore-volume effluent mineralized 64 percent of the remaining organic solutes (37 percent or 951 mg/L on the basis of raw retort water). This represents a total removal of 80 percent of the DOC by the sequential application of spent shale and biological oxidation. In addition, the cellular yields (g protein/mol C removed) from the shale-pretreated water were significantly higher than in control cultures of raw retort water (3.8 g/mol vs. 2.7 g/mol). This suggests that the

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spent shale may have reduced the osmolality or removed some of the toxic components from retort water thereby allowing the bacteria to expend less energy on maintenance and more on biomass production.

As predicted by equilibrium studies (Sakaji et al., 1982), the DOC removals by the column of spent shale were not sustained; only 21 percent of the DOC was removed from the third pore volume. Biooxidation of the third pore-volume of effluent mineralized 56 percent of the residual DOC (44 percent or 1060 mg/L on the basis of raw retort water); the overall DOC removal was 65 percent. The cellular yield was depressed compared with the yield from the first pore-volume of effluent (3.5 g/mol vs. 3.8 g/mol).

Spent shale removed both refractory and biodegradable compounds from the first pore-volume of effluent. Biological mineralization of DOC by control cultures was typically 1400 mg/L, whereas the acclimated inoculum succeeded in degrading only 951 mg/L from the shale-pretreated water. The remainder of the biologically available substrates were sorbed by the spent shale. For the third pore-volume of effluent, more of the biodegradable components of raw retort water remained in solution; 1060 mg/L of DOC was susceptible to biooxidation. Whereas pretreatment by spent shale allowed for higher cellular yields, it did not enhance biooxidation.

Distribution study. The DOC contents of the LpF and HpF were 55 and 45 percent, respectively. As discussed previously, approximately 50 percent of the DOC of raw retort water is consistently mineralized by exhaustive biological treatment. We have proposed (Jones et al., in press) that the majority of the biorefractory compounds in Oxy-6 retort water would be predominantly associated with the LpF and that the HpF would be the major source of carbon and energy for the microorganisms in unfractionated raw water. We postulated that spent shale, however, would preferentially sorb compounds from the LpF.

To substantiate the proposal that spent shale and biooxidation generally remove different classes of organic compounds, the ability of each treatment process to remove DOC from either the LpF or HpF of Oxy-6 retort water was investigated. The majority

of the biorefractory solutes appeared to be associated with the LpF, although each fraction supported microbial growth and neither fraction was totally degraded. Approximately three times more carbon was utilized from the HpF than from the LpF. This evidence supported our hypothesis that the biorefractory constituents were solutes less polar than fatty acids, such as nitrogen and oxygen heterocycles.

The results from a parallel set of experiments indicated that TOSCO II spent shale preferentially sorbed organic compounds from the LpF and had a very low sorptive affinity for the biodegradable polar components. The sorption of the LpF carbon was initially rapid; fifty-two percent of the LpF DOC was removed (Fig. 1). In contrast, virtually no sorption (3 to 4 percent) of the HpF occurred within 24 hours. The removals of DOC from the HpF were substantial, however, after 24 hours. This delayed response was probably a result of biodegradation by indigenous microbiota; aseptic conditions cannot be established or maintained without extensive physical or chemical modification of the shale. These findings supported the proposal that spent shale and biological oxidation are complementary processes for the treatment of Oxy-6 retort water. This has also been verified by the sequential application of the two processes; the DOC removal attributable to the individual
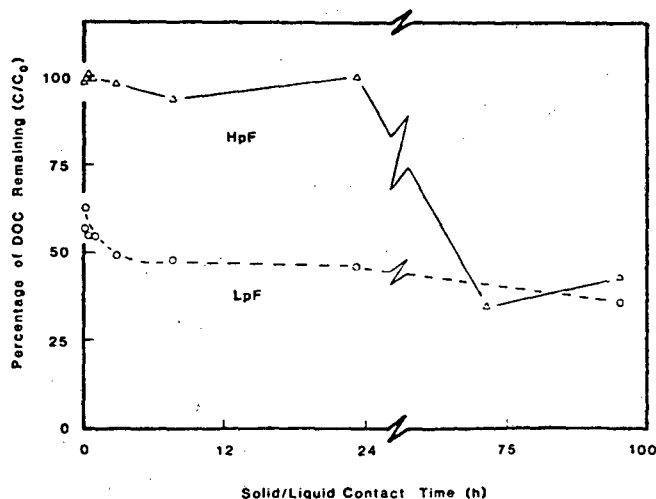

Figure 1. DOC Removal from Reverse-Phase Fractions of Oxy-6 Retort Water by TOSCO II Spent Shale; 60-80 mesh; 750 mg/mL

treatments is additive, regardless of the process sequence (Jones et al., 1982).

Combined sorbent-biotreatment study. The possibility of enhanced organic solute removal (i.e., the removal of DOC in excess of the sum of the individual DOC removals) by the simultaneous application of biological and sorbent (spent shale or PAC) treatments was investigated. Zimpro, Inc. (Anon., 1977) and other PAC manufacturers (see DeJohn and Black, 1980) have claimed that the addition of PAC will enhance the performance of activated sludge beyond that attributable to the sum of the treatments. Several mechanisms have been proposed to account for this synergistic effect. (i) The elimination of toxic constituents by adsorption would encourage development of a more prolific, diverse microbial community that can effect more extensive mineralization of the bioavailable compounds than the existing community (Lee and Johnson, 1979). (ii) The addition of carbon promotes the adsorption of organic substrates and permits the use of higher sludge ages in continuous-flow reactors. These combined effects may encourage more extensive conversion of refractory compounds (Lee and Johnson, 1979). As a corollary to this, compounds that are present in low concentrations may be sorbed to such a degree that the localized concentrations exceed the enzyme affinity constants and the previously unavailable organic compounds can be degraded. (iii) Microbial removal of adsorbed organic compounds from the surfaces of the organic carbon can effectively regenerate the surface and allow for further sorption (Grieves et al., 1977). (iv) The sorbent may provide attachment sites for microbial species that cannot survive in suspension but which may have exceptional abilities to degrade solutes that are unavailable to freely suspended cells. Based on these proposed mechanisms for combined sorbent-biological treatment, we investigated the effects of both powdered activated carbon and spent shale on the performance of biotreatment.

Contrary to predictions, a synergistic effect between sorbent and biooxidation was not observed (Fig. 2). Except for the highest shale dosage, the amount of DOC removed by combined sorbent-biological treatment was equal to the sum of the DOC removals from each individual process. The

increase in the degree of treatment with dosage appeared to be solely the result of increased available surface area. In contrast to industry's claims, other workers have observed this same result (DeWalle, Chian, and Small, 1977; Scaramelli and DiGiano, 1973). When two independent sets of data that purportedly support a synergistic effect between PAC and biotreatment (Kalinske, 1972; Lee and Johnson, 1979) are carefully examined, it becomes clear that the data fail to support the hypothesis. This confusion is a result of semantics, insufficient controls, and improper data manipulation. Many authors undiscerningly use the term "enhancement" to refer simply to the organic solutes removed by PAC addition to activated sludge and not to a synergistic removal afforded by an interaction between the two processes. Secondly, biological treatment often is directly compared with bio-PAC treatment without accounting for the independent sorptive effects of PAC (e.g., Grieves et al., 1977). Finally, care must be taken when percentages are compared. Grieves et al. (1977) concluded that PAC enhanced biotreatment by 50 to 60 percent when percentage removals by sequential and simultaneous treatments were compared. A reanalysis of the data, however, reveals only 22 to
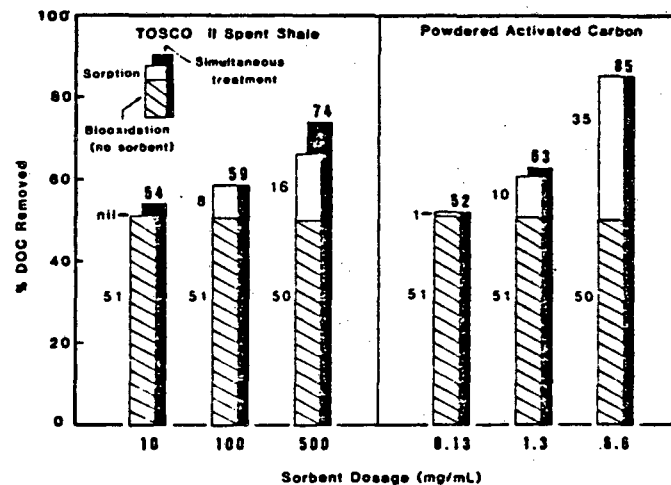
Figure 2. DOC Removal from Oxy-6 Retort Water: Separate and Combined Treatment by Sorption (TOSCO II Spent Shale and PAC) and Biooxidation; spent shale 60-80 mesh; PAC 12-40 mesh.

26 percent enhancement. Although theories about the enhanced effects of combined treatment are prevalent in industrial literature, few data are presented to document these claims. The lack of enhancement from the combined application of either spent shale or PAC and retort water, therefore, should not have been surprising since there is little evidence that this proposed phenomenon indeed exists.

Steam Stripper

A "pilot-scale" unit has been designed for evaluating steam stripping of dissolved gases from oil shale process waters under isothermal and adiabatic conditions. A primary design criterion was the ability to perform accurate material balances around the entire system. The evaluation of both process efficiency and the effect of steam stripping on subsequent treatments were major objectives. A reboiler configuration was not considered because intensive boiling of the bottoms could significantly modify the treated wastewater so that the results from subsequent treatment steps would be suspect. Steam stripping was preferred to air stripping because the stripping medium, water vapor, can be condensed and thereby separated from the noncondensable stripped gases (Sherwood, Pigford, and Wilke, 1975). Since steam stripping research within the petroleum industry indicates that the optimum operating temperature is 110 $^{\circ}$C (Manual on Disposal of Refinery Wastes, 1969), a pressurized system was essential. A schematic of this newly designed steam stripper is shown in Figure 3.

The major components are constructed of 316 stainless steel. The stripping column is a 4.88-m x 5.08-cm i.d. Pyrex beaded-glass tube
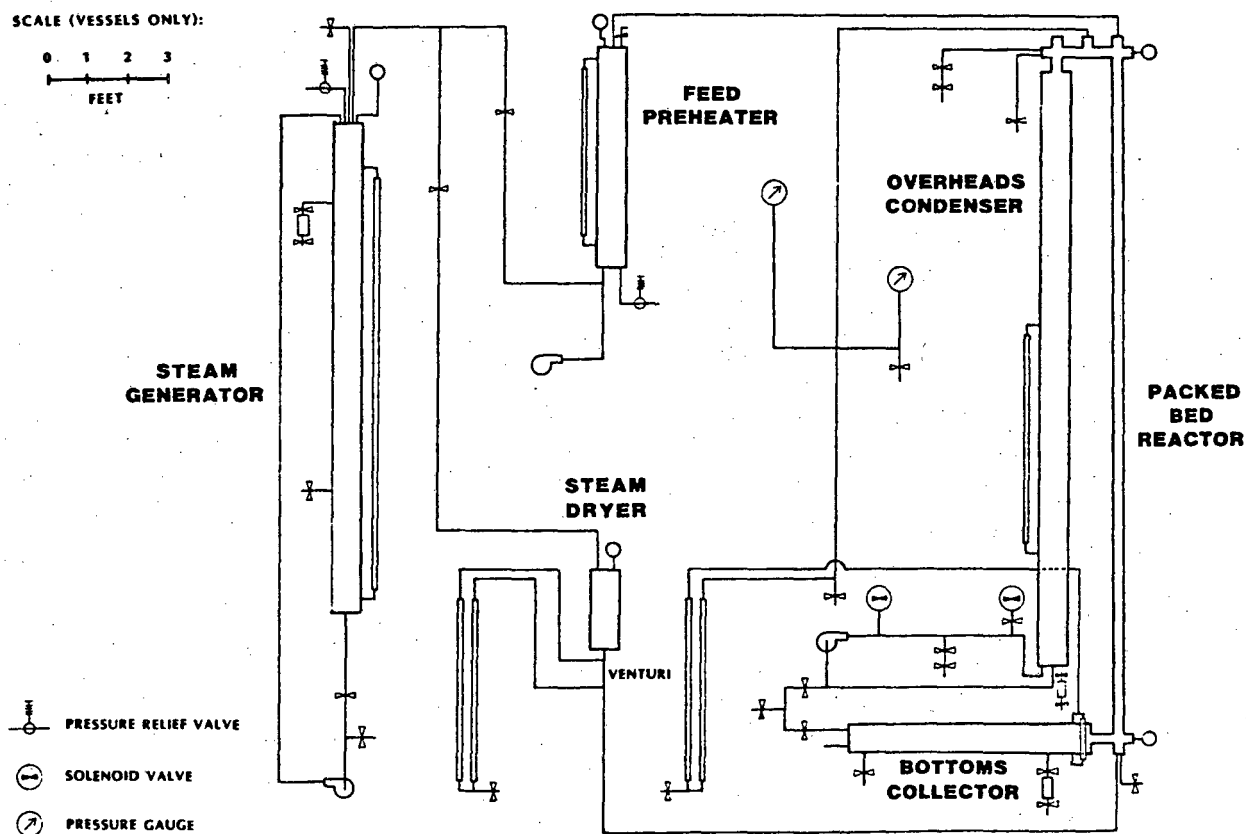

Figure 3. "Pilot-Scale" Steam Stripper: Schematic Diagram

packed with 0.64-cm Intalox ceramic saddles (Norton Ind., Irvine, CA). Wet steam is generated by a 6-kW flash evaporation unit and dried and superheated in a 6-kW steam drier. The dry steam is injected at the bottom of the packed bed. The temperature of the effluent gas streams, superheated steam, and wastewater influent are monitored and controlled remotely. The temperature gradient between the superheated steam in the column and the overheads condenser can be preset, and this gradient governs the flow rate of steam. The wastewater feed is preheated before injection at the top of the column to minimize the temperature difference between the liquid and steam phases. This configuration results in countercurrent flow of the steam and liquid streams. The treated wastewater is pooled in a bottoms collector, and the steam and stripped gases are collected in the overheads condenser.

The wall effects in the reactor column were minimized by choosing a ratio of packing material diameter to inside column diameter of a least 1 to 8. The length of the packed bed was chosen to minimize "end" effects caused by the dispersion of flow at the entrance and exit and to give a sufficient number of transfer units; the system was also designed to allow for variable bed heights. Condensation of the gas phase in the packed bed was minimized by wrapping the column with heating tape and fiberglass insulation. This was the only practical means of approaching isothermal and adiabatic operating conditions.

The ratio of steam to liquid flow rates governs the removal of the dissolved gases from the wastewater stream. While holding the liquid flow rate and packed bed height constant, the rate of dissolved gas stripping is ultimately determined by the temperature differential between the steam and overheads condenser. Increasing the steam to liquid ratio will increase the absolute removals, but efficient operation will necessarily require lower ratios. Optimized conditions will maximize the transfer efficiencies of contaminative solutes from the liquid to the steam phase (i.e., mole solute removed per mole steam) while allowing the bottoms to overheads ratio to approach the ideal (i.e., ensure complete separation and collection of the two phases). Isothermal and adiabatic

operating conditions are required to meet the latter goal.

UV/Ozonation Studies

Ozonation and UV irradiation were evaluated for treatment of biorefractory organic solutes in Oxy-6 retort water. Direct mineralization of DOC was determined for each method and for combined UV/ozonation, but emphasis was placed on the use of these methods to effect structural alterations which would promote subsequent biooxidation.

UV irradiation. Short exposure to intense UV radiation was insufficient to mineralize or alter the recalcitrant compounds in raw or spent retort water. The results of extensive UV irradiation of spent Oxy-6 retort water followed by biological treatment are presented in Figure 4. The lower graph is the cumulative UV energy supplied to the photoreactor. Each pair of bars
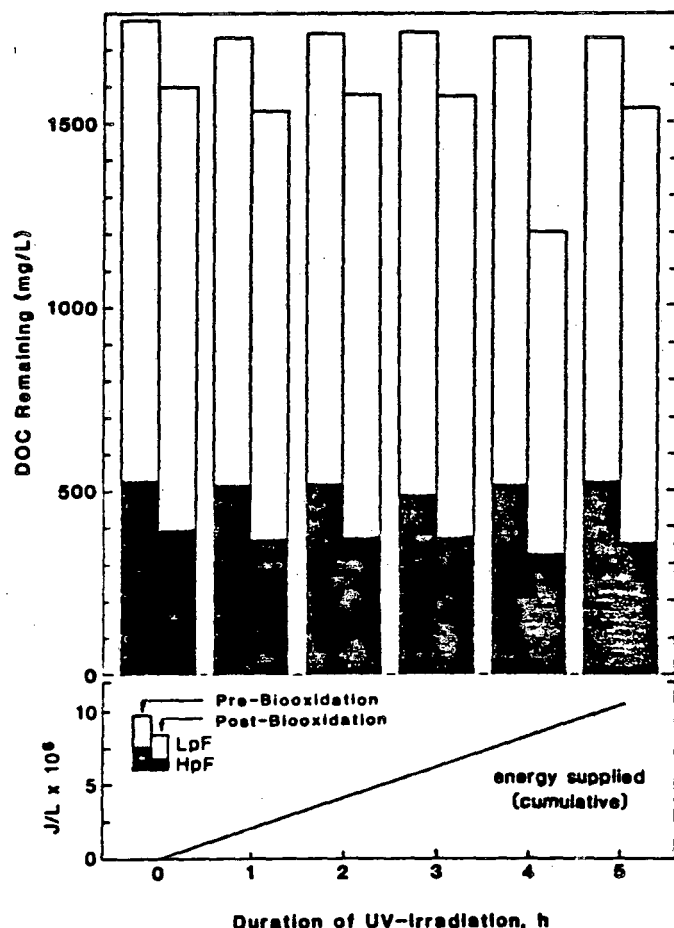

Figure 4. Biooxidation of UV-Pretreated Spent Oxy-6 Retort Water

represents a sample withdrawn from the reactor at hourly intervals. For each pair, the first bar is the DOC concentration that remained after UV irradiation, and the second bar is the DOC concentration after subsequent biological treatment. The solid portion of each bar is the DOC concentration of the HpF. Five hours of intensive ultraviolet irradiation of spent retort water did not mineralize a significant amount of DOC (2 percent), remove the chromophoric substances that give retort water its characteristic color, or change the relative polarities of the organic constituents. Furthermore, UV radiation did not appear to structurally alter the biorefractory organic compounds. Biooxidation subsequent to photochemical pretreatment did not mineralize additional carbon compared with nonirradiated reinoculated control cultures (i.e., the difference in DOC for each pair of bars was equivalent to the control).

The degradation of organic solutes by exposure to UV radiation is accomplished by (i) absorption of sufficient UV radiation to cleave intra-molecular bonds, producing lower-molecular-weight fragments, (ii) generation of organic free radicals, (iii) interaction of free radicals with oxygen to produce peroxy and hydroperoxy radicals, which are capable of subsequent reactions including the abstraction of hydrogen from organic substances and the generation of radical chain reactions (Crosby, 1972; Manny, Miller, and Wetzel, 1971; Plimmer, 1972), and (iv) photochemical excitation of molecular oxygen to produce the highly reactive singlet oxygen specie (Crosby, 1972). Ultraviolet irradiation of retort water may have been ineffective because of the presence of photo-oxidation inhibitors (see Larson, 1978). Particulate and colloidal carbonates can protect organic solutes from the effects of UV irradiation (Manny et al., 1971); the high concentration of carbonates in retort water may have prevented photoalteration.

Ozonation. Ozone applied to raw or spent retort water in low dosages for short periods was incapable of mineralizing a significant portion of the DOC or altering the structures of the biorefractory organic solutes. The effects of extensive ozonation of spent retort water are

represented (Fig. 5) in a manner analogous to Figure 4 except that the lower graph represents the cumulative amount of ozone consumed. The hourly ozone demand corrected for volume changes was also determined (Fig. 6). The ozone demand was greatest initially, steadily declined until the four-hour sample, and then appeared to increase slightly in the five-hour sample. This apparent increase may have been the result of an analytical error, incomplete mixing, or variations in the oxidative reaction rates. Although five hours of ozonation at 7.1 mg/L-min resulted in the consumption and solubilization of more than 1.6 g/L of ozone, only a slight amount of DOC mineralization (4 percent) was effected. The small fraction of compounds that were mineralized or altered by ozonation was responsible, however, for the majority of the color of spent retort water. The decrease in absorbance with treatment was most pronounced at 297 nm (Fig. 7).
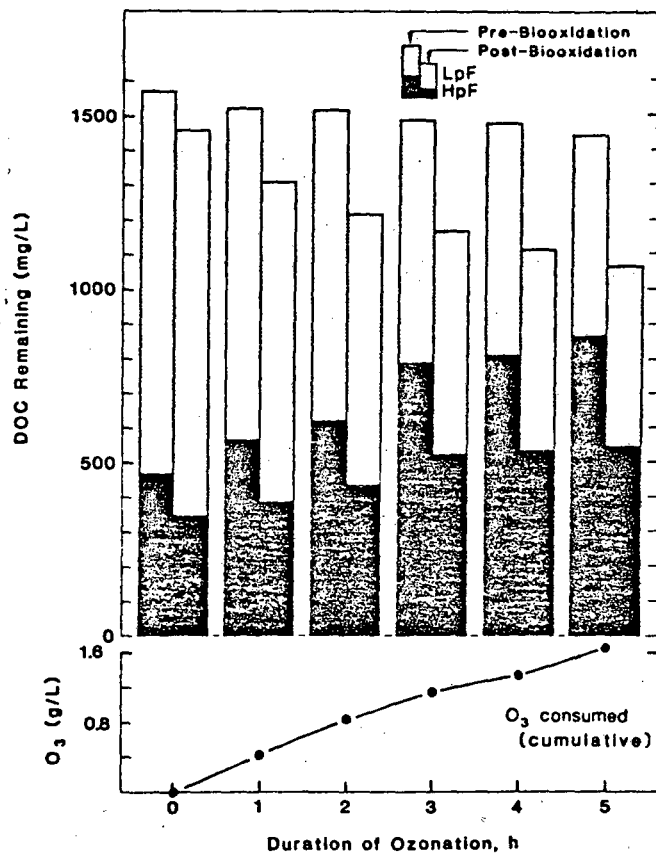

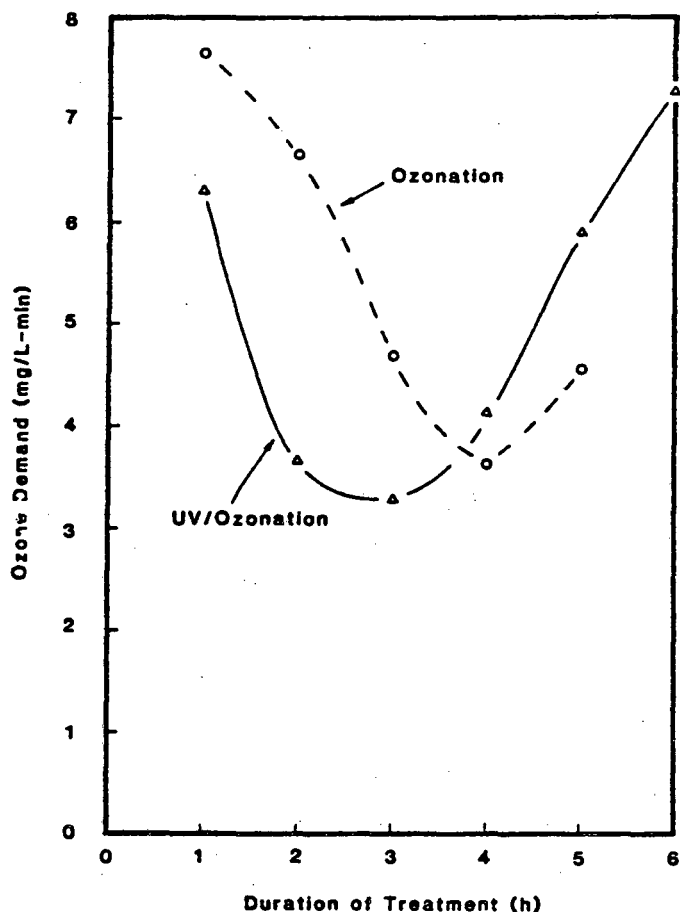Figure 5. Biooxidation of Ozone-Pretreated Spent Oxy-6 Retort Water

Figure 6. Ozone Demand During Ozonation and
Combined UV-Irradiation/Ozonation of Spent
Oxy-6 Retort Water

Figure 7. Effect of Ozonation and Combined
UV-Irradiation/Ozonation on UV Absorbance of
Spent Oxy-6 Retort Water

In contrast to small dosages of ozone used in the preliminary experiments, extensive ozonation of spent retort water altered a significant portion of the residual organic solutes; 14 percent of the DOC that was previously recalcitrant became amenable to microbial mineralization. Of the 380 mg/L of the DOC that was converted to structures that could be biologically oxidized, approximately 320 mg/L was at the expense of carbon in the HpF which was created by either ozonation of LpF carbon or alteration of refractory HpF carbon. Although the enhancement of biological mineralization was nearly exclusively at the expense of HpF carbon, the concentration of DOC in the HpF after biological oxidation of the five-hour sample was higher than that of the time zero, unozonated, biologically treated sample; a portion of the more highly oxidized products became less degradable.
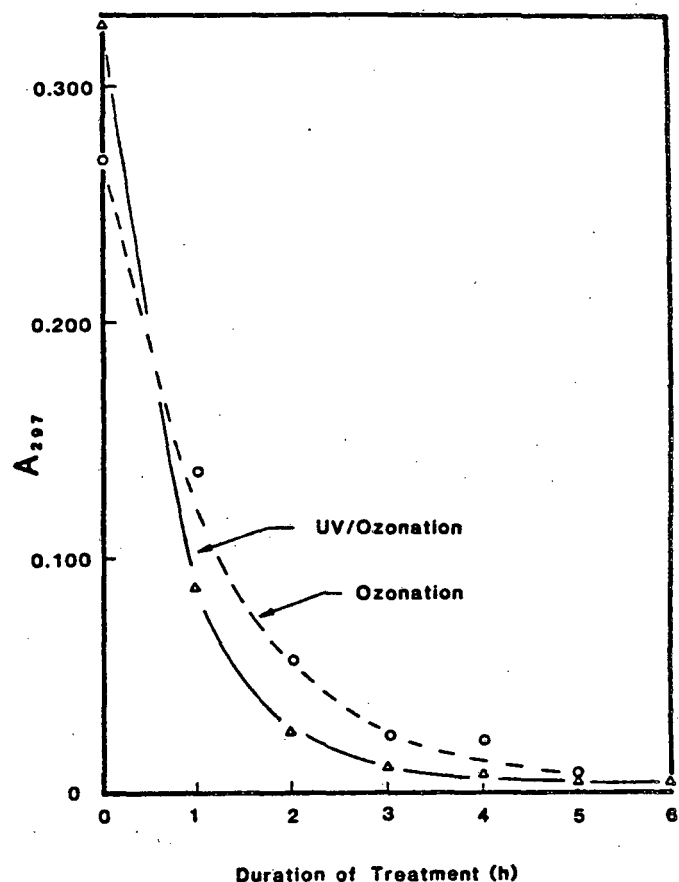
We have repeatedly noted that foaming is a major drawback to ozonation of raw retort water. This intense foaming was not evident, however, when spent retort water was ozonated. This change probably resulted from the microbial mineralization of aliphatic carboxylic acids, which can act as surfactants. In addition, the possibility of excessive consumption of ozone or free radicals by unprotonated ammonia or carbonate ions was minimized by (i) stripping ammonia from raw retort water by vigorous aeration during primary incubation in the fermentor (the ammonia concentration after 100 hours of incubation was reduced from 86 mM to less than 2 mM), and (ii) conducting the experiments at the unaltered pH of retort water, which is below 9.0.

In an aqueous medium, the oxidative ability of ozone appears to be dependent on pH, alkalinity,

and the organic and inorganic solutes. For acidic and neutral solutions (pH less than 9.0), ozone reacts predominantly as the parent ozone molecule; these reactions are relatively slow and highly specific, depending on the class of organic compound and bonding structure. In contrast, ozone in basic solutions (pH greater than 10.0) is catalytically decomposed by hydroxide ion to hydroxyl radical (OH·), the most reactive and effective oxidant known to occur in aqueous solutions (Hoigné and Bader, 1978; Larson, 1978), and superoxide ion (Bailey, 1982; Hoigné and Bader, 1976; Weber, 1972). The alteration of the refractory organic compounds and the elimination of the chromophoric substances were most likely a result of direct oxidation by the parent ozone molecule; the solution pH probably precluded the decomposition of ozone by OH⁻ into its highly reactive radicals. The susceptible solutes were gradually modified until the solution was devoid of these compounds; at that point ozone was no longer an effective oxidant.

Combined UV irradiation/ozonation.

The organic solutes in raw or spent retort water were resistant to mineralizaton by short exposures to low dosages of ozone in conjunction with UV radiation. Subsequent biooxidation was not improved by this pretreatment. In contrast, six hours of simultaneous ozonation and UV irradiation of spent retort water mineralized 20 percent of the organic carbon beyond the amount that initially could be biodegraded and appeared to significantly alter the remaining biorefractory compounds. The effects of extensive-UV/ozonation of spent retort water are represented (Fig. 8) in a manner analogous to Figure 4 except that the lower graph represents both the cumulative amount of ozone consumed and UV energy supplied.

Extensive UV/ozone treatment initially either mineralized the LpF organic solutes or transformed them into HpF solutes; oxidation of compounds would be expected to increase their polarity. After three hours of treatment, the LpF carbon continued to be mineralized, but further conversion to the HpF carbon pool was not observed. The intense color of the spent retort water was almost entirely eliminated. The decrease in absorbance at 297 nm as a result of UV/ozonation occurred more quickly

and was more pronounced than with ozonation alone (Fig. 6). In addition, the persistent, distinctive odor of the water was reduced to almost undetectable levels.

Three hours of intensive ozonation coupled with UV irradiation also effected considerable structural alterations of the organic solutes in spent retort water. An acclimated microbial seed was capable of utilizing approximately 400 mg/L of DOC that was normally unavailable in completely spent retort water prior to physicochemical treatment. This auxilary biooxidation was entirely at the expense of newly created HpF organic compounds. Biodegradability of retort waters seems to correlate with increasing content of HpF organic carbon (Daughton et al., 1982). The composition of the water following the serial application of biooxiation, three hours of UV/ozonation, and exhaustive secondary biological treatment was similar to that of spent water after five hours of ozonation followed by biotreatment.
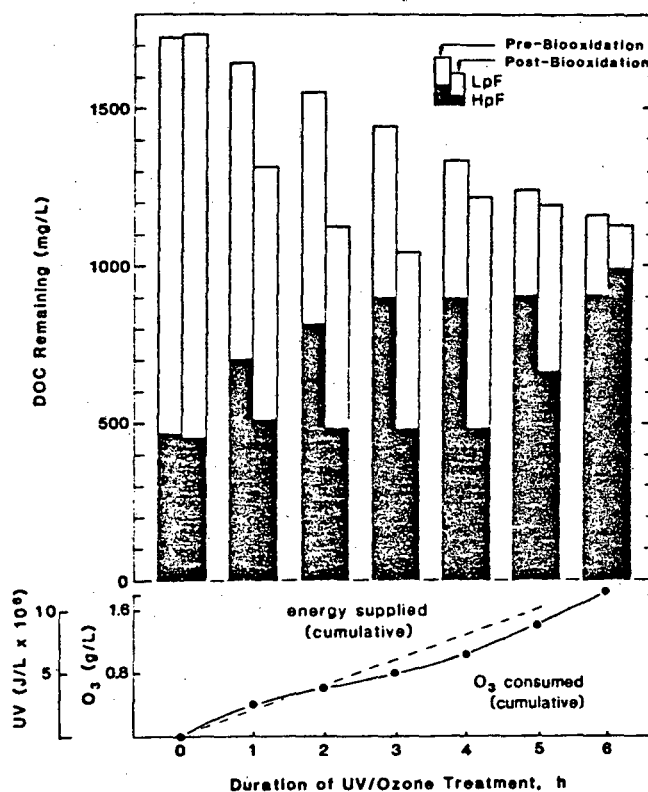

Figure 8. Biooxidation of UV/Ozone-Pretreated Spent Oxy-6 Retort Water

Simultaneous UV/ozone treatment of spent water beyond three hours of exposure resulted in a reversal of the trend of increasing biodegradability with increasing dosage. New HpF carbon was not being generated, and the HpF that remained appeared to become more refractory to the microbial inoculum. After six hours of combined UV/ozone treatment, only one percent of the DOC was susceptible to microbial attack, yet the majority of the solutes that remained after biooxidation was HpF carbon. In fact, for the six-hour sample, the portion of HpF was larger after biological treatment; the bacteria were growing at the expense of the LpF carbon and altering a portion of this carbon to refractory HpF compounds. Microbial incompetence may not have been the only factor limiting the degradation of the remaining solutes; increased toxicity or the lack of a specific nutrient or cofactor essential for the decomposition of the newly created solutes may have limited further mineralization of the DOC.

Ozone consumption appeared to decline more rapidly for the simultaneous UV/ozone treatment process (Fig. 6) compared with unassisted ozonation. After three hours, however, the ozone demand suddenly increased, and after six hours reached a level equal to the one-hour demand. This initial decline, followed by an increasing demand, may have been a function of several features of ozone chemistry. Ultraviolet radiation catalyzes the decomposition of ozone into OH· (Bailey, 1982; Prengle and Mauk, 1978; Sierka and Cowen, 1980) and superoxide ion, and promotes the production of free organic radicals (Prengle et al., 1975). A possible explanation for the fluctuating ozone demand is that the initial reactions resulted from oxidation by the parent ozone molecule because UV radiation could not sufficiently penetrate the solution to decompose the ozone into its radical components. After three hours, the color of the solution was significantly reduced, and UV radiant energy might then have been able to interact with ozone to create hydroxyl radical, which rapidly and nonspecifically altered the remaining compounds. This explanation could account for both the increase in ozone demand and the qualitative changes that were observed in the residual solutes.

Combined UV irradiation/ozonation has been reported to be superior to either of the individual treatments for the elimination of refractory organic impurites from water and for the treatment of industrial wastewaters (Bailey, 1982; Hoigné and Bader, 1976; Kuo, Chian, and Chang, 1977). Perhaps the major drawback to this approach as a pretreatment for biooxidation of oil shale wastewaters is that both ozonation and UV irradiation/ozonation create multiple products from each oxidizable compound (Hoigné and Bader, 1976; Kolonko et al., 1979). This plethora of oxidation products is especially significant for oil shale wastewaters, which are characterized by large numbers of substituted heterocycles present in extremely low individual concentrations. Although UV irradiation/ozonation may generate more degradable solutes, it may actually exacerbate the existing problem of enzyme specificity and threshold concentration effects (Daughton, unpublished observations).

Extensive UV irradiation combined with ozonation effected mineralization of a substantial portion of the DOC after six hours, but further biological treatment was unsuccessful. Although color and odor could be nearly eliminated, 41 percent of the DOC of raw retort water remained after exhaustive serial treatment by primary biooxidation, UV/ozonation, and secondary biooxidation. The organic solutes that remained appeared to be refractory to both chemical and microbial oxidative alteration or mineralization; physicochemical methods that effect complementary treatment will be required to upgrade oil shale wastewaters for reuse or codisposal.

SUMMARY

DOC removals by spent shale and PAC complemented the effects of biological degradation of the organic solutes in Oxy-6 retort water. Sequential treatment by spent shale followed by biotreatment offered up to 80 percent reduction in DOC concentration. Enhanced treatment by the simultaneous application of sorbent and biooxidation was not observed.

Steam stripping of oil shale process waters may enhance biological treatment by reducing ammonia toxicity and by relieving enzyme

inhibition. A pilot-scale unit has been designed to evalute steam stripping of dissolved gases from these wastewaters under isothermal and adiabatic conditions.

UV irradiation was an ineffective oxidant; following five hours of irradiation, organic solutes in spent retort water remained unavailable to acclimated bacteria. In contrast, extensive ozonation mineralized four percent of the DOC and altered 14 percent of the remaining organic solutes. It was postulated that the observed alterations were a result of the highly specific parent ozone molecule. The effect of ozone on spent retort water solutes appeared to be enhanced and accelerated by UV radiation; this was probably the result of UV-catalyzed disproportionation of ozone into highly reactive decomposition products. More than 41 percent of the DOC remained, however, following primary biooxidation, UV/ozonation, and exhaustive secondary biotreatment.

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