

# A PRELIMINARY EVALUATION OF OIL SHALE WASTEWATER TREATMENT BY OZONE AND ACTIVATED CARBON

Raymond A. Sierka  
Professor, Department of Civil Engineering  
and Engineering Mechanics  
The University of Arizona  
Tucson, Arizona 85721

## A B S T R A C T

Oil shale processing wastewaters are laden with a wide spectrum of inorganics and organics and will require treatment either before disposal to the environment or reuse within the process. The treatment of two modified in-situ retort oil shale wastewaters by ozonation and activated carbon has been studied. In addition, the effect of sequencing these unit processes has been investigated. The study indicated that activated carbon-ozonation is the preferred treatment sequence. Organic loadings on activated carbon were reduced after ozonation of retort wastewaters. Solution pH was shown to effect the rate of total organic oxidation.

### INTRODUCTION

Western United States oil shales are envisioned as future replacements for conventional fossil fuels. Currently, technology exists which could be utilized to recover approximately 600 billion barrels of oil (EPA Oil Shale Research Group, 1980).

Oil from shale is produced by thermal degradation of kerogen in retorts situated either above ground or in situ. Surface retorting is a three-step procedure involving shale mining, size reduction and heating in above-ground retorts. In-situ retorting is a batch operation which begins with permeability modification of the shale bed then in-place heating. If after the rock is fractured a portion is mined prior to heating, then the process is termed as modified in-situ retorting.

The most probable Western United States shale deposits to be recovered initially are located in the Green River Basin of Colorado, Utah and Wyoming. This resource is positioned in a watershed containing the Colorado River, which is oversubscribed in the Lower Basin and therefore the question of water availability to support this industry is posed. Conversely, since between 15.1 and 3,482.5 liters (ℓ) of wastewater are generated in the production of one barrel of oil from shale (Farrier, 1978), it should be considered as a potential process water supply to alleviate water shortages and, if not, then a

treatment must be applied prior to discharge into the environment to amend the wastewater's pollution character. There is, for example, concern that a number of the pollutants may be carcinogenic, mutagenic and teratogenic.

Oil shale processing wastewaters are laden with a wide spectrum of inorganics and organics, some in high concentrations. Further, this chemically complex wastewater has been difficult to characterize because techniques either have not been developed or constituents exceed the published concentration limits for a given analytical procedure resulting in possibly inaccurate results (Fox, 1978).

One potential use of oil shale wastewaters is spent shale wetting and compaction and yet even for this proposed use the State of Colorado has decreed that organic removal must precede use (Fox, et al., August, 1980).

The approaches employed for inorganic pollutant removal include use of activated alumina absorption, precipitation with phosphoric acid and lime (Mercer, 1978), ion exchange and stripping. Organics removal by physical, chemical and biological processing techniques such as activated carbon and polymeric resin adsorption, air stripping (Harding, 1978 and 1977), reverse osmosis and electro dialysis (Water Purification Assoc. Qtrly Status Report, May-August 1979), as well as aerobic and anaerobic treatment (Yen, 1980) have been studied.

This research centered on the removal of organics from wastewaters produced in two modified in-situ retorting processes by a combination of ozone oxidation and activated carbon adsorption. Also, the effect of sequencing the unit processes of adsorption and oxidation was investigated.

The first wastewater treated was generated in Occidental Petroleum Company's Retort 6, a modified in situ retort.

A history statement for the process water samples (Division of Environmental Sciences, Laramie Energy Technology Center) has been reported. During this research, only Sample Point 2 - Tank 6 water,

hereinafter referred to as OXY-6 wastewater, was employed. Table 1, (Analysis Statement for OXY-6 Process Waters) is a partial chemical characterization of this composited wastewater which was collected from February through May 1979.

TABLE 1  
Chemical Characterization of OXY-6 and R-17 Oil Shale Wastewaters

Parameter (mg/l)*	OXY-6		R-17	
	Range	Mean	Range	Mean
Sodium	2300-2800	2600	250-290	270
Potassium	92-130	104	15-16	16
Magnesium	2.2-5.5	3.6	9.5-10.0	9.8
Calcium	7.6-12.0	11.0	6.5-8.2	7.6
Barium		0.5		
Cadmium		0.1		
Chromium		0.1		
Lead		0.5		
Chloride	370-490	392	2090-2260	2190
Fluoride	29-32	31	7.3-7.5	7.4
Nitrate (N)	2700-7600	2160	7700-10,000	8900
Sulfate	1380-1480	1430	1550-2330	1860
Carbonate	1300-1700	1480	1080-1250	1130
Bicarbonate	5500-6200	5800	5760-6100	5910
Nitrogen (NH <sub>3</sub> )	1000-1300	1320	1000-1300	1340
Oil & Grease	95-1900	391	380-2300	1020
Total Dissolved Solids (180°C)	8200-9700	8900	4430-6240	5150
Hardness as (CaCO <sub>3</sub> )			60-60	60
Total Alkalinity (as CaCO <sub>3</sub> )	7100-7400	7190	5920-6840	6690
pH (Standard pH Units)	8.32-8.85	8.54	8.65-8.65	8.55
Conductivity (µmhos at 25°C)	13,300-13,300	13,300	17,500-17,500	17,500
Chemical Oxygen Demand	13,300-18,300	14,300	11,300-13,300	13,700
Total Carbon	2610-5220	4040	4468-5963	5026
Total Inorganic Carbon	340-1200	1040	1058-1250	1156
Total Organic Carbon	1500-4380	2890	3245-5666	3910

\* Except where noted.

From the data, it can be seen that this process water is moderately high in pH containing high concentrations of organics, as measured by total organic carbon (TOC) and chemical oxygen demand (COD), and inorganics such as sodium, ammonia, carbonates and bicarbonates.

The second wastewater was derived from the Laramie Energy Technology Center total shale oil/process water products, produced during Run 17 of their 150-ton capacity, simulated in situ retort (150T-SISR). A total description (History Statement for the 150T-SISR-R17 Process Water Sample, April 8, 1980) of the retorting parameters and sample collection has been reported. Table 1 is a partial chemical characterization of the unfiltered and composited samples [79-(150T-SISR-R17)-OOW-UO1] employed in this research and hereinafter designated as R-17. This water is moderately high in pH, and contains high concentrations of sodium, chloride, nitrate, sulfates, carbonate, bicarbonate and ammonium, as well as COD and TOC.

The third wastewater was double-steam stripped R-17 (hereinafter termed R-17-DSS) produced at the Department of Chemical Engineering at the University of Wyoming (personal communication, Prof. A. L. Hines).

## EXPERIMENTAL

Removal of organic matter from oil shale wastewater can be achieved by a variety of techniques including oxidation and adsorption. To access the ability of activated carbon and ozone to cause removal of organics from oil-shale wastewater, two sets of experiments were conducted. In the first series, OXY-6, R-17 and R-17-DSS (R1-A, R2-A, and R3-A) wastewaters were ozonated and then subjected to activated carbon treatment. The reverse procedure, (R1-B, R2-B and R3-B) that is, activated carbon treatment preceding ozonation, was then carried out in an effort to optimize the sequence of these treatment techniques. Table 2 is an outline of the experimental plan.

TABLE 2

Experimental Plan Treatment Sequence

Run No.	Substrate Type	Treatment Sequence
R1-A	OXY-6	Ozone → Activated Carbon
R1-B	OXY-6	Activated Carbon → Ozone
R2-A	R-17	Ozone → Activated Carbon
R2-B	R-17	Activated Carbon → Ozone
R3-A	R-17-DSS	Ozone → Activated Carbon
R3-B	R-17-DSS	Activated Carbon → Ozone

### Ozonation

All ozonations were carried out in a 6.0 inch ID diameter by 18 inch high pyrex glass reactor in the semi-batch mode (continuous gas admission, static liquid volume). Ozone and its carrier gas was admitted to the reactor through a 316 type sintered stainless steel sparger which was of donut design with an O.D. of 5.0 inches while the I.D. hole was 1.5 inches. The average gas bubble size produced was 5 µ.

Ozone was generated from pure oxygen delivered from cylinders at 10 psig to the OREC ozonator model 03B1-0. Three gas flow rates, 1/8, 2.1, and 6.2 l O<sub>2</sub>/min were employed and the ozonator produced respectively 106, 120 and 222 mg O<sub>3</sub>/min. The variable gas flow rates were necessary due to the moderate to severe foaming problem encountered with the various wastewaters employed.

Samples were generally removed from the reactor at the following times: 0, 30, 60, 90, 120, 180 and 240 minutes, and analyzed for TC and TOC. Additionally, pH and total alkalinity by titration with HCl to pH 4.3 were measured for the influent and 240 minutes ozonated samples.

### Activated Carbon Adsorption

For Runs 1A, 2A and 3A, after 240 minutes of ozonation, a 200 ml aliquot of treated wastewater

was placed in a sealed flask and contacted with 2.5 g/l of Carborundum 1240 powdered activated carbon (PAC) which had been prepared by the manufacturer from the granular form. The suspension was agitated on a shaker table for 2.0 hours. Previous experience had indicated that adsorption equilibrium would be achieved within 60 minutes. The PAC was separated from the liquid by vacuum filtration through a Millipore 0.45  $\mu$  filter. Equilibrium TOC and TC concentrations were obtained on the filtrate by injecting samples in duplicate into the Dohrman DC80 Organic Carbon Analyzer. TC analysis on the samples did not require sample pretreatment; however, TOC analysis required acidification (three drops of phosphoric acid in a 15 ml sample) and stripping with zero grade nitrogen gas for three minutes prior to injection into the Dohrman DC80.

When adsorption preceded ozonation (i.e., Runs 1B, 2B and 3B), 2.5 g/l of Carborundum 1240 was mixed with approximately 3.0 l of shale oil wastewater. The 3 l suspension was mixed by a three-inch magnetic stirring bar in a 4 l erlymeyer flask for a 2.0 hour period. Following vacuum filtration through an 0.45  $\mu$  Millipore filter, the filtrate was ozonated for 4.0 hours.

Equilibrium isotherm testing of R-17 and OXY-6 waters before and after 4.0 hours of ozonation was also accomplished. For these runs, 200 ml volumes of sample were mixed for 2.0 hours with various masses of Carborundum 1240 PAC ranging from 500 mg/l to 5,000 mg/l. TC and TOC were measured by a Dohrman DC80 on 0.45  $\mu$  filtered samples as described above.

## RESULTS AND DISCUSSION

The primary thrust of this research was to examine the effect of ozone oxidation and activated carbon adsorption on the removal of organics and inorganics from oil shale wastewater; OXY-6, R-17 and R-17-DSS. Also, the effect of sequencing these unit processes was examined to determine the optimum treatment.

### OXY-6 Treatment

A summary of the experimental results is presented in Table 3 which lists the TC and TOC data as a function of reaction time. Also included is the total ozone admitted to the reactor at the various reaction times.

In R1-A, 2.5 l of OXY-6 wastewater was ozonated for the first ten minutes of the run at a rate of 106 mg O<sub>3</sub>/min. Immediately, the batch foamed voluminously and for the first ten minutes of reaction, the foam escaped the reactor with the ozone/oxygen gas and was collected in an open beaker. The total volume of foam, after collapse, was 160 ml. It should be noted that the foam was continuously being contacted with ozone/oxygen gas leaving the reactor through a tygon reactor vent line and therefore, treatment continued. After ten minutes of reaction, the ozone rate was increased to 120 mg O<sub>3</sub>/l min and remained at this level for 20 minutes.

Initially, the foam in the reactor contained two layers with a dark-brown color phase positioned over a lighter, tan color. The liquid portion of the batch was dark brown in color, but turned lighter with ozonation time until after 240 minutes of reaction the turbid liquid was light-green in color.

TABLE 3

Total Carbon and Total Organic Carbon Removal  
By Ozone Oxidation and Activated Carbon Adsorption

Reaction Time (min)	R1-A			R1-B			R2-A			R2-B			R3-A			R3-B		
	$\Sigma$ Ozone Admitted to Reactor	TC*	TOC*	$\Sigma$ O <sub>3</sub>	TC	TOC	$\Sigma$ O <sub>3</sub>	TC	TOC	$\Sigma$ O <sub>3</sub>	TC	TOC	$\Sigma$ O <sub>3</sub>	TC	TOC	$\Sigma$ O <sub>3</sub>	TC	TOC
	0	0	3652	2836	0	3652	2836	0	3948	3121	0	3948	3121	0	1878	1823	0	1878
After PAC (2.5 g/l)	0	NA	NA	0	3060	2334	0	NA	NA	0	3198	2485	0	NA	NA	0	1387	1388
30	3,460	3563	2814	3,600	2903	2252	3,530	3470	2817	3,600	2903	2380	6,600	--	--	3,600	1291	1303
60	10,120	3245	2669	10,260	2682	2073	7,130	3267	2883	7,200	2709	2308	13,320	1684	1654	9,750	1234	1270
90	16,780	3095	2538	16,920	2443	1904	13,790	3184	2824	10,800	2527	2243	19,980	1609	1619	16,410	1187	1205
120	23,440	3004	2446	23,580	2185	1717	20,450	3141	2769	17,460	2386	2070	26,640	1547	1588	23,070	1136	1124
150	36,760	--	--	36,900	1841	1487	33,770	3037	2607	30,780	1774	1733	39,9990	--	--	36,390	--	--
240	50,080	2823	2343	50,220	1399	1136	47090	2907	2525	44,100	1616	1582	53,280	1296	1304	49,710	632	656
After O <sub>3</sub> Plus PAC (2.5 g/l)	--	2532	2095	--	NA	NA	--	2247	2180	--	NA	NA	--	1003	994	--	NA	NA

\* All TC and TOC values reported in mg/l

After 30 minutes of ozonation the collapsed foam (160 ml) was re-injected into the batch and the ozonation rate increased to 222 mg O<sub>3</sub>/min.

From Figure 1 it can be seen that the rate of TOC removal was greater for the first half of the run than the last half. For example, the TOC decreased from 2,836 mg/l to 2,446 mg/l during the first 2.0 hours, but only from 2,446 mg/l to 2,343 mg/l during the last 2.0 hours of reaction.

These data indicate the production of ozone resistant partial oxidation products during the early stages of ozonation. After 4.0 hours of ozonation, the treated wastewater was shown to be amenable to adsorption by activated carbon since the TOC was further reduced to 2,095 mg/l from 2,343 mg/l after contacting with 2.5g/l of Carborundum 1240.

The companion run to R1-A was R1-B. Treatment commenced by contacting the "as received" OXY-6 wastewater with 2.5 g/l of Carborundum 1240 for 2.0 hours then filtering the batch to remove the activated carbon. This process reduced the TOC from 2,836 mg/l to 2,334 mg/l which is lower than the final effluent from R1-A.

Ozonating the PAC-treated wastewater caused a further reduction in TOC from 2,334 mg/l to 1,136 mg/l.

Comparing the total reduction in TOC in R1-A and R2-A, it can be seen from Table 3 that 493 mg/l and 1,198 mg/l were removed by ozone treatment respectively.

As with R1-A, the final color of R2-B was light green; however, the foam produced in this run ranged from light tan to white.

#### R-17 Treatment

In the second series of runs, R-17 wastewater was the substrate. The first batch treated was 2.5 l of R2-A. This dark-brown colored liquid foamed even more effusively than R1-A. The rate of ozone added was 106 mg O<sub>3</sub>/min for the first five minutes, followed by 55 minutes of ozonation at 120 mg O<sub>3</sub>/min and finally 222 mg O<sub>3</sub>/min over the next three hours.

For the first 13 minutes of the run, foam exited the reactor. When collapsed, the total foam amounted to 1,200 ml of liquid. At 30 minutes into the run, ozonation was temporarily suspended and the 1,200 ml of foamate added to the reactor and ozonation re-started. Once again, foaming was intense, resulting in a collapsed foam volume from the reactor of 780 ml over the next 30 minutes of ozonation. As described above, the collapsed foam was readmitted to the reactor after 60 minutes of ozonation. Foam carryover for a third time then occurred; however, this time only 280 ml of collapsed foam was collected after 30 additional minutes of ozonation. This liquid was reinjected into the reactor and no further foam escaped, although it was present in the reactor mass.

Foam coloration in this batch was similar to R1-A that is brown, then tan and white with the latter color predominating.

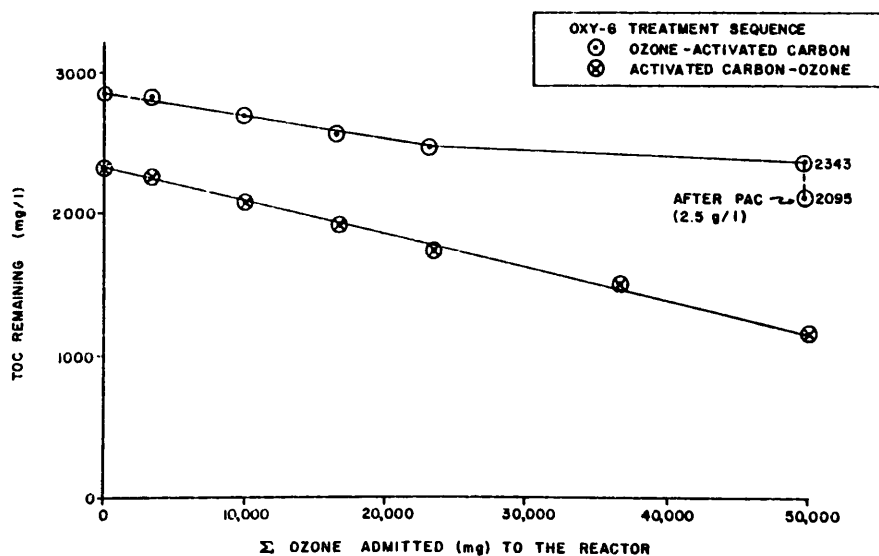


FIGURE 1  
TOC REMOVAL AS A FUNCTION OF OZONE ADMITTED TO THE REACTOR

The TOC reduction data plotted in Figure 2 indicated two distinct responses occurring during the first hour and last three hours of ozonation. Overall, the influent TOC was decreased from 3,121 mg/l to 2,525 mg/l.

Activated carbon treatment reduced the TOC by 345 mg/l to 2,180 mg/l for the 4.0 hour ozonated R-17 wastewater.

In R2-B, the wastewater received activated carbon pretreatment prior to ozonation. The result was adsorption of 636 mg/l of TOC. Subsequent ozonation led to foaming and a small amount (144 ml) of foam being transported out of the reactor to the collection beaker. No foam left the reactor after 18 minutes of ozonation.

The color of the foam ranged from dark brown at the commencement of the run and progressed to a tan and finally an off-white color. At times during the run all three colors were present in the foam, but gradually the dark-brown, then the tan color disappeared, leaving on the off-white color foam.

The liquid portion of the batch changed from a dark-brown to a light, greenish tint. The liquid was turbid.

After 4.0 hours of ozonation the TOC decreased from 2,488 mg/l to 1,582 mg/l. These data are displayed in Figure 2 from where it can be seen that after 30,780 mg O<sub>3</sub> had been admitted to the reactor, the rate of TOC destruction decreased slightly.

Comparing TOC removal by ozonation (Table 3) it is seen that in R2-A, ozonation caused the destruction of 596 mg/l of TOC while in R2-B, 903 mg/l of

TOC was removed. In terms of TOC removal by PAC, in R2-A, 345 mg/l was adsorbed by the adsorbent while in R2-B, the decrease in TOC due to Carborundum 1240 was 636 mg/l. The total removals of TOC in R2-A was 941 mg/l and for R2-B it was 1,539 mg/l.

#### R-17-DSS Treatment

The substrate for the R3-A and R3-B was R-17 which had received double steam stripping (R-17-DSS). This process removed 42% of the TOC from R-17 and in doing, so decreased the foaming potential of the wastewater. In R3-A foam escaped from the reactor in amounts less than previously experienced with R2-A; however, the fact that foam left the reactor at all can be attributed to the high gas flow rate (i.e., 6.2 l/min) and ozone mass flow rate of 222 mg O<sub>3</sub>/min employed. In R3-B for the first 35 minutes only, 120 mg O<sub>3</sub>/min of ozone was admitted at a gas rate of 2.1 l/min and these conditions only produced a minute amount of foam which exited the reactor.

At the end of the R3A, the liquid had changed from a dark-brown to light green, while in R3-B, the brown disappeared leaving a colorless solution which at ten minutes prior to the cessation of the ozonation, turned pink. When the ozonation was stopped the pink color disappeared. No apparent reason for the color change can be offered.

In R3-A the TOC removal after 4.0 hours of ozonation was 519 mg/l. Treatment by activated carbon reduced the TOC by an additional 310 mg/l to 994 mg/l as seen in Figure 3.

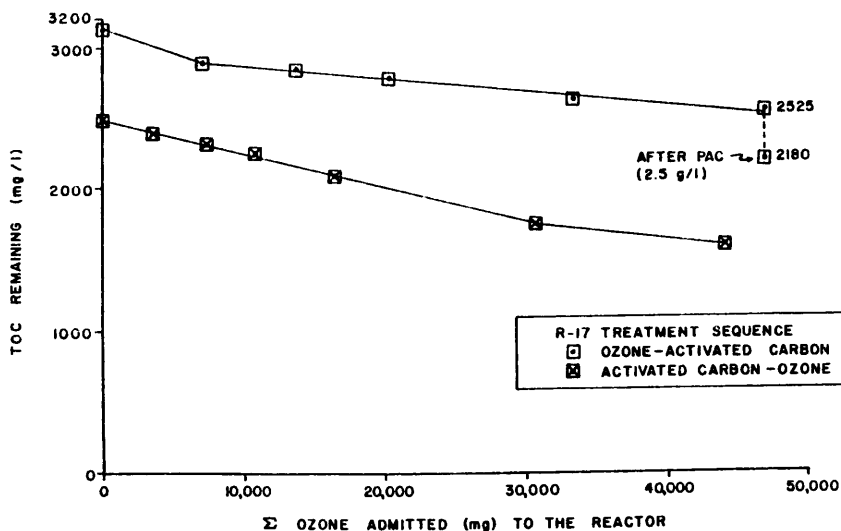


FIGURE 2  
TOC REMOVAL AS A FUNCTION OF OZONE ADMITTED TO THE REACTOR

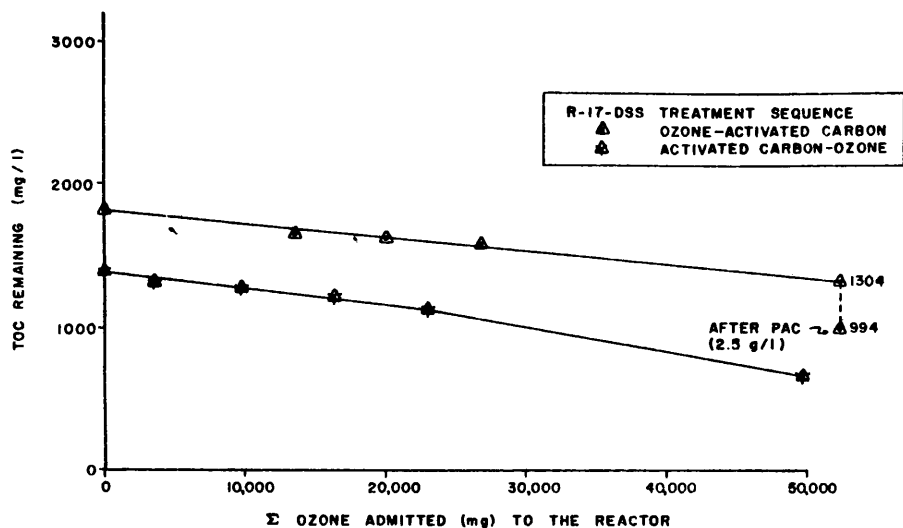


FIGURE 3  
TOC REMOVAL AS A FUNCTION OF OZONE ADMITTED TO THE REACTOR

R3-B received treatment by activated carbon first resulting in a TOC reduction of 435 mg/l and after ozonation the TOC remaining was 656 mg/l.

In analyzing the data presented in Table 4 it is readily apparent that ozone utilization in terms of TOC and TC destruction is maximized when activated carbon treatment precedes ozonation for each of the three wastewater types investigated.

TABLE 4

Ozone Utilization in TOC and TC Destruction

Run No.	Total mg Ozone Added Δ TOC (mg/l)	Total mg Ozone Added Δ TC (mg/l)
R1-A	101.6	60.4
R1-B	41.9	30.2
R2-A	79.0	45.2
R2-B	48.8	27.9
R3-A	102.7	91.6
R3-B	67.9	65.8

The first reason for these responses is the fact that when activated carbon precedes ozone, it is presented with the total spectrum of organics present in the wastewaters at high concentrations. The classes of compounds readily adsorbed are nonpolar entities which are difficult to oxidize with ozone. Since the ozone oxidizes the remaining organics easily and more completely, the TOC will be reduced and the amount of ozone required will also be reduced.

A second reason for these responses is partially found in the total alkalinity data listed in Table 5. For example, during R1-A, the influent had an alkalinity of 7,044 mg/l which was reduced to 5,297 mg/l over the 4.0 hours of ozonation. In R1-B, the influent total alkalinity was reduced to 6,652 mg/l after treatment with activated carbon; however, after 4.0 hours of ozonation, the residual total alkalinity

was considerably reduced to 2,006 mg/l. In both runs pH changes were moderate: 8.79 to 8.66 for R1-A and 8.79 to 8.71 for R2-B.

TABLE 5

Total Alkalinity and pH Data  
On Treated OXY-6, R-17 and R-17-DSS

Run No.	R1-A	R1-B	R2-A	R2-B	R3-A	R3-B
pH						
Influent	8.79	8.79	8.50	8.50	7.50	7.50
Effluent	8.66	8.71	7.46	6.40	1.83	1.83
Total Alkalinity (mg/l)						
Treatment						
None	7044	7044	6209	6209	548	548
Ozone (4.0 hrs)	5097	NA	1224	NA	0	NA
Ozone (4.0 hrs) + PAC (2.5 g/l)	3865	NA	1124	NA	0	NA
PAC (2.5 g/l)	NA	6652	NA	5739	NA	642
PAC (2.5 g/l) + Ozone	NA	2006	NA	508	NA	0

The rate of organic oxidation by ozone is a function of ozone mass transfer from the gas phase to the liquid phase and the rate of ozone decomposition to free radicals. Oxidation by the ozone molecule, O<sub>3</sub>, is a slow, highly selective process, which generally exhibits a first order response with respect to solute. "Radical" type reactions occur after ozone has decomposed to free radicals. Oxidation reactions of this type are characterized as, being extremely fast and indiscriminate. High pH favors the decomposition of ozone to free radicals but carbonates and bicarbonates are known scavengers (Hoigne, et al., 1978) of ozone free radicals. Since peroxy and hydroperoxy free radicals are more powerful oxidants than ozone itself, anything which tends to reduce their concentration, such as alkalinity, would decrease

the rate of organic total oxidation and thus increase the requirement for ozone.

In R2-B again pretreatment with activated carbon causes a reduction in total alkalinity from 6,209 mg/l to 5,739 mg/l. After ozonation for 4.0 hours, however, the remaining alkalinity is greatly reduced to 508 mg/l. The batch pH was reduced from 8.50 to 7.46 during the run. In R2-A, approximately the same amount of alkalinity is removed by ozonation that is 6,209 mg/l to 1,224 mg/l, yet on the average more alkalinity was present in the reactor during ozonation than in R2-B. A drop in pH to 6.22 was noted for this batch from an initial value of 8.50.

Comparing the alkalinity change in R1-A and R2-A by activated carbon, it can be seen that in the former case, alkalinity was reduced by 1,432 mg/l and only 100 mg/l in the latter run.

The substrates for R3-A and R3-B were double steam stripped R-17 and in the course of their production, the total alkalinity was reduced to 548 mg/l and the TOC by 42%. Ozonation of R3-A led to the production of acidic partial oxidation products which reacted with the carbonates and bicarbonates permitting the batch pH to be reduced as volatile acids were stripped out of solution. In fact, within 30 minutes, the batch pH had been lowered to 2.80 which is far less than the  $pK_a$  value of  $H_2CO_3$  and thus  $CO_2$  was oxygen-stripped from the aqueous phase. The low solution pH was detrimental to the ozone oxidation of the organics present in the wastewater since ozone autodecomposition to free radicals is catalyzed by hydroxyl ions. This is reflected in the

average 102.7 mg  $O_3$  required to decrease 1.0 mg/l of TOC in R3-A.

The pretreatment by activated carbon in R3-B apparently increased the total alkalinity of the batch; however, as in R3-A, the pH dropped quickly to less than 2.0 and ultimately reaching 1.83 after 4.0 hours of ozonation.

The amount of ozone required to reduce 1 mg/l of TOC in R3-B was 67.9 mg compared with 102.7 mg in R3-A. Once again the beneficial effects of adsorption are seen.

Examining the TC and TOC data in Table 3 for these two runs shows that little difference exists between these two parameters after at least 30 minutes of ozonation. This can be interpreted that all the inorganic alkalinity has been stripped from solution and the remaining dissolved carbon was organic in nature.

To quantify the effect of solution pH on ozone, auto-decomposition and system kinetics, a third ozonation run on double steam stripped R-17 was carried out. To this 2.5 l batch (R3-C) was added NaOH to raise the pH to 9.0 and then boric acid and K Cl ( $\approx 1.0N$ ) to buffer the solution. The results of this run are plotted in Figure 4 together with the data from R3-A.

During R3-C, the pH of the batch dropped from 9.03 to 8.37 even though it was buffered, indicating the production of acidic by-products and alkalinity stripping. The data in Figure 4 reveal that, as expected, the amount and rate of oxidation increased as seen by the decrease in TOC by 745 mg/l as compared

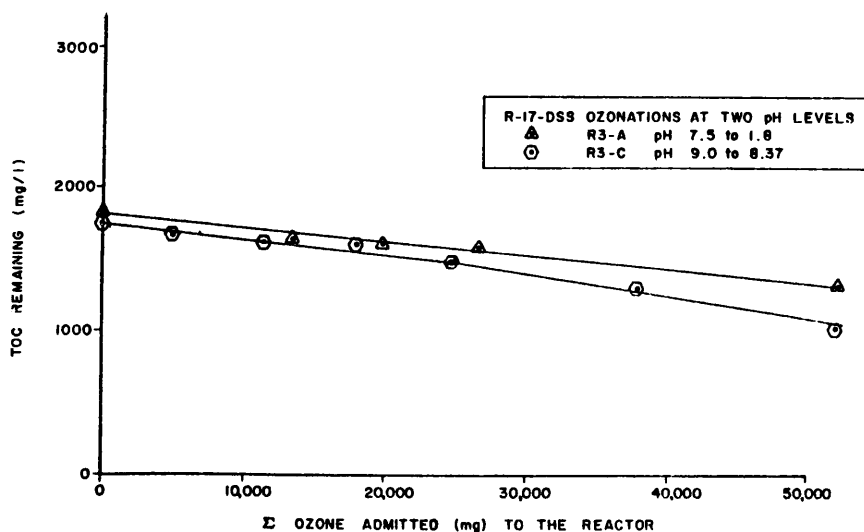


FIGURE 4  
TOC REMOVAL AS A FUNCTION OF OZONE ADMITTED TO THE REACTOR

with only 519 mg/l in R3-B. In terms of ozone utilization, R3-C required 62.6 mg O<sub>3</sub> to remove 1.0 mg/l of TOC while in R3-B, 102.7 mg O<sub>3</sub> were required. Again, these data reflect the fact that ozone free radicals are more effective in totally oxidizing organic carbon in shale oil wastewaters.

The second major reason why activated carbon pretreatment prior to ozonation produces an effluent lower in organic content and is the preferred routing is found in the data listed in Table 6.

TABLE 6  
Adsorption Isotherm Data on OXY-6 and R-17 Oil Shale Wastewaters Before and After Ozonation

PAC (mg/L)	OXY-6		R1-A		R-17		R2-A	
	TOC (mg/L)	X/M (mg/mg)	TOC (mg/L)	X/M (mg/mg)	TOC (mg/L)	X/M (mg/mg)	TOC (mg/L)	X/M (mg/mg)
0	2836	--	2343	--	3122	--	2525	--
500	2568	0.536	2175	0.336	2794	0.556	2305	0.450
1000	2563	0.273	2176	0.167	2630	0.492	2308	0.217
2500	2203	0.253	2063	0.112	2457	0.266	2200	0.122
5000	1969	0.173	1965	0.076	2137	0.197	2052	0.395

The adsorption isotherm data reveal that higher loadings (i.e., X/M) occur when either untreated OXY-6 or R-17 is the substrate than when these wastewaters had been ozonated for 4.0 hours prior to activated carbon treatment.

Primarily the reason for the decreased loadings is the fact that ozonation causes the partial oxidation of some dissolved organics leading to, in general, structures which are more highly oxygenated and thus more polar. Increased polarity leads to a decrease in adsorption on the adsorbent.

#### SUMMARY

This research has shown that oil shale wastewaters can be treated by ozone oxidation and activated carbon to remove dissolved organic carbon as measured by TOC. Sequencing of these two unit processes is important with activated carbon preceding ozonation as the preferred routing.

Higher loading of the adsorbent was achieved before ozonation of each substrate than after ozonation and this is attributed to the production of polar partial oxidation products by ozone.

Ozone utilization efficiency in the reactor is enhanced when the substrate is pretreated with activated carbon and again this is due to the fact that the adsorbent removed nonpolar compounds which are more difficult to completely oxidize with ozone than polar structures.

The removal of pollutants from oil shale retort waters has been studied by a number of researchers employing a wide variety of techniques. None of

these treatments individually has been successful. Combinations of unit-processes will be required; however, proper sequencing will determine the efficiency of the process. For those systems employing activated carbon and ozone oxidation, this is particularly important.

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