

## METHOD FOR RECLAIMING WASTE WATER FROM OIL-SHALE PROCESSING

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### INTRODUCTION

Because the importance of industrial pollution abatement continues to grow, this work was initiated to develop possible solutions for environmental problems that an oil-shale processing industry may create (1).<sup>1/</sup> Although the commercial production of fuel from oil shale is still in the future, it is realized that adequate disposal of waste products from a large oil-shale processing plant may present major problems. The Bureau of Mines, U.S. Department of the Interior, has initiated research to identify and propose solutions for the waste disposal problems in advance of industrial development as a guide to the incorporation of environmentally acceptable disposal processes in future plants.

The major waste products produced by an oil-shale processing industry are large quantities of spent shale, process gas, and process water. Because the process water formed during the production of shale oil contains considerable quantities of soluble organic and inorganic materials, it will present a major disposal problem.

The actual amount of water produced and the degree to which it is contaminated will depend upon the type and operating condition of the retorting process used and the nature of the oil shale. The amount of process water formed may equal 20 to 40 percent of the oil produced. This means that a plant producing 100,000 barrels of oil per day may also produce from 20,000 to 40,000 barrels of contaminated waste water that will require treatment before it can be used or discharged to the environment.

This paper describes a method for successively removing the contaminants so that water of different qualities may be obtained at the end of each step in the process. Hence, if water needs only partial treatment for plant use, the purification process may be stopped at any step.

Because most of our oil shale is located in arid country, possibly all of the retort water produced will be reclaimed and used to extinction, thus eliminating the necessity for discharge to the environment. Deciding factors in selecting the method described were (1) to use materials that can be regenerated or discarded, and (2) to try to obtain a product or products that may be of value to offset the reclaiming costs.

The method found to be the most promising makes use of a combination of (1) chemical treatment with lime to remove carbonates, most of the ammonia, and a portion of the organic materials; (2) adsorption on activated carbon to remove the remaining organic material; and (3) cation and anion exchange resins to remove the balance of the cations and anions.

### EXPERIMENTAL

Process water produced by the Bureau's Gas Combustion Retort No. 2 operated by the Colorado School of Mines Research Foundation, Rifle, Colorado (2), and water

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<sup>1/</sup> Underlined numbers in parentheses refer to items in the list of references at the end of this report.

that separated from shale oil obtained by in situ retorting near Rock Springs, Wyoming (3), were studied. The process waters were obtained from the bottoms of the oil storage tanks after settling from the shale oils. Residual suspended oil was allowed to separate further from the waters in separatory funnels, and the waters were drained off. The remaining suspended oil and suspended solids were removed by filtering through water-wet filter paper. The filtrates were highly colored solutions of organic and inorganic materials.

Two slightly different water treatment methods were used. In the first method, Step A, sufficient lime to release the ammonia in the water plus a 10 percent excess was added to 1 liter of the colored, filtered water, and the mixture was boiled with constant stirring for 1 hour. This precipitated some of the organic material and essentially all of the carbonates, and liberated most of the ammonia. In Step B, the water, still colored, was passed through a column of activated carbon (Calgon Corporation, Filtrasorb 300),<sup>2/</sup> 2.5 cm in diameter by 100 cm long. The effluent from the carbon-packed column was colorless and clear. In Step C, the water was passed through a 2.5 cm by 80 cm column of cation exchange resin (Rohm and Haas IRC-84). This removed the ammonium and other cations by exchanging them for hydrogen ions, which changed the pH of the water from basic to acidic. In Step D, the water was passed through a similar column of anion exchange resin (Rohm and Haas IR-45). This replaced the anions with hydroxyl ions to produce a relatively pure effluent.

In the second method, Steps A and B were reversed. The organic material was removed by passing the colored filtrate through the activated carbon column first, and the lime and ion exchange resin treatments followed.

The effectiveness of removing the soluble organic material was estimated by color reduction and carbon analysis by a Beckman Model IR-315 Infrared Carbon Analyzer. Activated carbon removed essentially all of the soluble organic material (4). Ion analyses were made by standard chemical and instrumental methods.

## RESULTS AND DISCUSSION

The gas combustion retort water was selected for this study because it contains more total dissolved components than any other water tested, and it was produced by a process likely to be used in the future. The in situ water was selected because of its special origin and its high sodium, carbonate, and chloride ion content.

Analytical results for waste waters derived from Colorado and Wyoming oil shale produced by gas combustion and in situ retorting, respectively, show the presence of essentially the same components. However, the amounts and proportions of the components can vary widely.

The components include both organic and inorganic compounds. The organic material consists of amines, acids, bases, and neutral compounds. The actual number of organic compounds expected to be found in process water could be in the hundreds, but no specific compound identifications were made in the current study. The bulk of the inorganic components consists of ammonium, sodium, bicarbonate, carbonate, sulfate, and chloride ions. While the ions listed are not all of the ions in the water, they are the major ones. Spot analyses showed that minor ions were decreased in proportion to the others and generally were eliminated completely.

Tables 1 and 2 give the concentrations of the principal inorganic ions found in the two waters used and the concentrations remaining after the application of

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<sup>2/</sup> Reference to specific brand names is made for identification purposes only and does not imply endorsement by the Bureau of Mines.

each step of the two treatment methods. The ammonia concentrations of 8.91 and 4.80 grams per liter may be sufficiently high for economic recovery.

Table 1 shows the effectiveness of the two methods in removing the following ions from gas combustion retort water: ammonium, sodium, carbonate, chloride, and sulfate. Both methods removed these ions to an acceptable level with one pass (5, 6). The main advantages of Method 1 over Method 2 are emphasized in Step A (columns 1, 3, and 4). When the water was treated with lime first, 7.77 grams per liter (87%) of the ammonium ion, 12.78 grams per liter (88%) of the carbonate ion, and 3.20 grams per liter (59%) of chloride ions were removed from the water. When the water was passed over activated carbon first, the carbon removed 2.44 grams per liter (27%) of the ammonium ion, 1.92 grams per liter (13.3%) of the carbonate ion, and 0.32 gram per liter (5.9%) of the chloride ion. In general, the final products from both methods are comparable, but since treating the water with lime first (Method 1) is more economical because it reduces the load on the activated carbon and ion exchange resins, this method will be selected for future study.

In column 5, the sulfate values are inconsistent, particularly in that there appear to be more sulfate ions in the water after it is passed over the activated carbon in both methods. This could be caused by converting soluble sulfur-containing ions to sulfate but will require further study. The pH values shown in column 6 are all basic with the exception of Step C where the water was passed over the cation exchange resin. At this point in the process, the cations are exchanged for hydrogen ions and the pH changes to acid. This change in pH from basic to acidic causes unstable sulfur-containing ions to decompose. In so doing, free sulfur is precipitated, and the solution becomes cloudy in appearance. The removal of this finely precipitated sulfur presents a problem. It is too fine for filtration and settles very slowly. Flocculants may be useful, but they have not yet been investigated.

Table 2 shows similar results obtained for a water produced by in situ retorting near Rock Springs, Wyoming. The sodium, carbonate, chloride, and sulfate contents of this water are particularly high, but the process appears to work equally well on this water and, in general, the comments concerning table 1 are applicable to table 2.

In both methods, the ions were decreased successively in steps. The first method is preferable because its final product generally has slightly lower ion contents for each ion considered. Also, by treating the water with lime first to remove most of the ammonium, carbonate, and other ions present, along with some organic material, the load on the activated carbon and ion exchange resins is reduced. This will substantially reduce the cost of the treating process. Ion reductions of 90 percent and better were obtained by one passing, and this should be sufficient for most water uses. Further purification can be accomplished by utilizing a second set of ion exchange resin columns.

#### CONCLUSION

The procedure described can be used to reclaim waste water from oil-shale processing by (1) treating the water with lime, and heating to remove ammonia, carbonates, and some organic material; (2) passing over activated carbon to remove the balance of the organic material; and (3) passing over ion exchange resins to remove anions and cations. The effluent from any step can be diverted for plant use where further purification is not necessary. It may be possible to recover from this process ammonia and ammonium salts.

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REFERENCES

1. Holcomb, R. W. Science, v. 169, July 1970, pp. 457-459.
2. Ruark, J. R., H. W. Sohns, and H. C. Carpenter. BuMines Rept. of Inv. 7303, 1969, 109 pp.
3. Burwell, E. L., H. C. Carpenter, and H. W. Sohns. BuMines Tech. Prog. Rept. 16, 1969, 8 pp.
4. Rizzo, J. L., and R. E. Schade. Water and Sewage Works, August 1969, pp. 307-312.
5. Committee on Water Quality Criteria, Federal Water Pollution Control Adm., Dept. of the Interior. Water Quality Criteria, 1968, 234 pp.
6. State Water Quality Control Board (California), Water Quality Criteria. Publication No. 3-A, 1963, pp. 258-273.

TABLE 1. - Removal of components from gas-combustion process water by methods 1 and 2

Method	6					
	1 Ammonium, g/l	2 Sodium, g/l	3 Carbonate, g/l	4 Chloride, g/l	5 Sulfate, g/l	pH
Untreated water	8.91	1.04	14.44	5.43	1.68	
1 Step						
A Lime treatment	1.14	1.02	1.66	2.23	1.48	9.70
B Over activated carbon	.57	.63	.42	1.52	1.90	9.10
C Over cation exchange resin	.11	.15	.65	.35	.77	2.40
D Over anion exchange resin	.00	.06	.18	.01	.00	9.34
2 Step						
A Over activated carbon	6.47	.77	12.52	5.11	2.71	8.72
B Lime treatment	1.73	.73	.89	1.14	.57	12.11
C Over cation exchange resin	.52	.28	.52	1.12	.76	1.35
D Over anion exchange resin	.50	.27	.08	.03	.10	9.29

TABLE 2. - Removal of components from in situ retort process by methods 1 and 2

Method	6					
	1 Ammonium, g/l	2 Sodium, g/l	3 Carbonate, g/l	4 Chloride, g/l	5 Sulfate, g/l	pH
Untreated water	4.80	3.10	19.22	13.41	4.45	
1 Step						
A Lime treatment	.52	2.83	5.26	3.11	3.98	8.79
B Over activated carbon	.33	2.03	4.36	2.22	1.18	9.08
C Over cation exchange resin	.25	.55	.57	.81	2.90	3.98
D Over anion exchange resin	.12	.48	.27	.38	.64	11.24
2 Step						
A Over activated carbon	4.03	2.63	6.70	10.37	3.69	8.76
B Lime treatment	1.41	2.14	.82	4.54	3.32	9.53
C Over cation exchange resin	.25	.58	.46	.88	2.84	4.07
D Over anion exchange resin	.21	.56	.50	.75	3.11	11.20