POTENTIAL TOXIC EFFECTS ON AQUATIC BIOTA FROM OIL SHALE DEVELOPMENT

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ABSTRACT

Research designed to assess potential impacts of effluents resulting from oil shale development on the aquatic biota has been in progress for two years. Primary objectives are: (1) to establish the extent to which these effluents can contaminate the aquatic system; (2) to characterize the chemical constituents entering the aquatic system; (3) to identify the principal toxicants present in the effluents with emphasis on the aquatic biota; and (4) to determine the transformation and transport behaviors of the toxic entities. Results of studies carried out on retorted oil shale leachates are discussed.

INTRODUCTION

The overall objective of this investigation has been to provide predictive information about the effects of pollutants derived from oil shale processing on surface waters and the aquatic biota.

The research plan embodies three areas of investigation: (1) chemical characterization of effluents and byproducts associated with the above energy development area; (2) field surveys and analyses of aquatic organisms in streams which are, or may be, impacted by these effluents; and (3) laboratory bioassays of known and potential toxicants associated with these effluents.

The major sub-objectives of this investigation are:

a. To establish data bases of biological and chemical information for evaluating the effects on water resources and ecosystems of potential toxicants from oil shale development.
b. To characterize the chemical components of products and byproducts for the purpose of identifying toxicants and potentially toxic substances which may reach aquatic ecosystems.
c. To determine the acute and chronic toxicity, including bioaccumulation, to aquatic organisms of chemicals and contaminants resulting from oil shale development.
d. To determine routes of transport of toxicants and potentially toxic substances between their sources and aquatic systems; mechanical parameters which define these routes and control rates and amounts of transfer; and the chemical/biological changes which occur.
e. To synthesize information, resulting from this and other studies, so that recommendations may be made to minimize the possible impacts on aquatic resources and ecosystems.

To date, the investigation has placed emphasis on the chemical and toxicological characterization of effluents derived from oil shale processing. Although attention could rationally be focused on process water derived from the retort, or leachates which result when retorted oil shale is exposed to water, only the latter have been investigated to date. The results of these studies, discussed below, should be regarded as preliminary in nature and representative of only the retorted oil shale studied.

RESULTS AND DISCUSSION

It appears that the presently preferred oil shale processing configurations are the in situ and modified in situ methods. In such instances, the majority of the retorted oil shale (ROS) will remain underground where ground waters, if present, can have direct access to it. If these ground waters gain access to the surface, they may carry the constituents leached from the ROS to surface waters. Thus, chemical and biological characterization has concentrated on leachates obtained from the large lysimeters located at Anvil Point, Colorado, which are filled with ROS from the Paraho operation (Berg 1977). Relatively large quantities of effluent water were collected from these during the summer and fall of 1977.

Chemical Characteristics

Chemical analyses of 150 leachate samples, collected over a period of approximately two months, have shown that the chemical characteristics of the leachates remained reasonably constant even though fairly large volumes of water passed through the lysimeters. Levels of more common chemical characteristics are summarized in table 1. Evaluation of these data indicates that the principal contributions to the dissolved solids concentrations originate from the dissolution of sodium and potassium salts with lesser contributions from calcium and magnesium salts. In order of relative concentration, the primary soluble ions present appear to be thiosulfate, sulfate, chloride, nitrate, and fluoride. The alkalinity of the irrigation water is also increased by dissolution of carbonates and bicarbonates but this is not striking. Perhaps the most unique characteristic of these leachates is the presence of high thiosulfate concentrations. Since thiosulfate disproportionates, as the aqueous medium becomes more acid, to form sulfate, the actual concentrations of sulfate and thiosulfate may be influenced by the pH of the system as well as relative concentrations of the parent salts. In any case, the presence of thiosulfate accounts for the high chemical oxygen demand of the leachates. Moreover, because thiosulfate forms stable, soluble complexes with several heavy metals, it may influence the solubilities of these metals.

Table 1. General water quality levels for common constituents in retorted oil shale leachates.

Parameter	Observed Range*
pH	10-11.2
Specific Conductance (μmhos)	11,000-18,000
Hardness (as $CaCO_3$)	400-1,200
Alkalinity (as $CaCO_3$)	200-400
Dissolved Solids	10,000-30,000
Calcium	60-550
Magnesium	10-300
Sodium	600-7,000
Potassium	100-1,000
Chloride	40-150
Fluoride	2-20
Nitrate	5-50
Sulfate	1,000-18,000
Thiosulfate	1,000-20,000

*Ranges observed for >100 samples from eight different ROS lysimeters each representing a different slope/packing configuration and each sprinkler irrigated. All concentrations in mg/l unless otherwise noted.

The leachate samples collected have also been analyzed for trace elements. Approximate mean values and ranges observed are summarized in table 2. Concentrations of several elements are notably high when compared with levels characteristic of natural surface waters for As, B, Li, Mo, Ni, Se, and Sn. The possible significance of these higher concentrations, in terms of possible effects on plants and animals, should be considered.

The aqueous leachates have also been examined on a preliminary basis for the presence of soluble organics. Ultraviolet-visible and infrared absorption spectrophotometric measurements, coupled with liquid chromatographic analyses, have shown that several types of organics are present.

Table 2. Trace element levels in retorted oil shale leachates.

Element	Approximate Mean, μg/l	Range, μg/l
Aluminum	800	70-2,500
Arsenic	80	70-150
Beryllium	<10	<10-48
Boron	1,000	350-2,300
Cadmium	<25	<25-80
Chromium	<25	<25-80
Copper	<25	<25-180
Iron	<20	<20-9,000
Lead	<100	<100
Lithium	10,000	50-20,000
Manganese	200	<50-800
Mercury	0.5	0.1-1
Molybdenum	100	<50-600
Nickel	120	<25-200
Selenium	110	100-150
Silicon	9,000	1,000-20,000
Strontium	5,000	1,000-20,000
Tin	100	30-4,500
Zinc	20	<5-1,400

Gas chromatographic analyses of the aqueous leachates, benzene extracts of these, and of air-evaporated leachates taken up in benzene, gave no indication of detectable amounts of organic compounds which could be chromatographed at temperatures up to 400°C on a 1.5% Dexil-300 column. Liquid chromatographic behaviors of the water-soluble compounds were generally indicative of conjugated and/or aromatic compounds. It was further shown that the concentration of total fluorescible material in these leachates was typically equivalent to approximately 1-10 mg/l. Present efforts are devoted to the identification of the primary organic compounds (or compound types) present.

Biological Characteristics

General evaluation of ROS leachates, in terms of biological effects, has been based on acute (96-hour), static bioassays carried out at the Fisheries Bioassay Laboratory, Montana State University. Two species were used: *Daphnia pulicaria* (water flea) and *Pimephales promelas* (fathead minnow) were used; the first, representing a "typical" invertebrate, the second, fish. These tests have provided estimates of the volumes of ROS leachates that cause 50 percent mortality when added to the test waters. These will be referred to as the Least Dilution-50 (LD50 in ml/l) values herein.

Static tests, run on eight different ROS leachates for 96 hours, indicated LD50 values, ranging from approximately 4 to 8 ml/l, for both *Daphnia* and fathead minnows. However, it was noted that dissolved oxygen levels in the test systems dropped to less than one part per million in nearly all instances for which leachate was added at levels exceeding ∿2 ml/l. While several contaminants present in the leachates may have contributed directly to the mortality observed, the reduction in dissolved oxygen was considered the most probable cause. This reduction was largely due to redox reactions, involving the rather large concentrations of thiosulfate present.

Subsequently, 30-day static bioassays (partial chronic) were run on fathead minnows in which the test tanks were continuously aerated to maintain dissolved oxygen levels. Under these circumstances, LD50 values increased to the 250-500 ml/l range. Thus, when depletion of dissolved oxygen was circumvented, toxic response was also reduced in magnitude in terms of both concentration and time.

These observations suggest two general conclusions: (1) the presence of thiosulfate has a deleterious effect, manifested primarily by a reduction in dissolved oxygen which can cause a toxic response in invertebrates and fish, and (2) when depletion of dissolved oxygen is circumvented, other leachate constituents appear to operate individually or in combination to induce mortality. In the latter instance, much higher leachate concentrations and longer exposure times are required to cause death. These results are limited in nature and are regarded by the authors as strictly preliminary. Further studies are in progress to define (if possible) the causative agents and the general universality of the cause and effect relationship for ROS from various processes.

SUMMARY

The above results indicate that several types of constituents may be leached from ROS. Some of those which may degrade surface and ground waters and have deleterious effects on aquatic biota may be inferred from the data obtained to date. These are thiosulfate, As, B, Mo, Ni, Se, and Sn. The limited bioassay results tend to support this contention in general terms. In this context, now, it appears that allowing ROS leachates to gain direct access to surface waters would be ill-advised. However, ultimate conclusions regarding the potential effects of ROS leachates on natural waters and resident aquatic biota must also be based on the answers to other questions including the following:

1. What leachate constituents affect the biota?
2. What are the environmental lifetimes, degradation products, and environmental parameters influencing lifetimes or degradation pathways?
3. Can the causative constituents gain access to surface waters?

The continuing thrust of this investigation is to address these questions.

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REFERENCES

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