United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S7-81-081 May 1981

EPA

Project Summary

Assessment of Oil Shale Retort Wastewater Treatment and Control Technology—Phases I and II

J. R. Klieve, G. D. Rawlings, and J. R. Hoeflein

Oil shale retorting is a synthetic fuel production technology on the verge of commercialization in the United States. In order to ensure that the emerging oil shale industry will have minimal adverse effects upon surface and/or groundwater where recoverable reserves of oil shale are found, demonstrated technologies to upgrade oil shale wastewaters must be available to developers. To this end, the U.S. Environmental Protection Agency has contracted with Monsanto Research Corporation (MRC) to conduct a three-year, five-phased study to: (1) summarize known information concerning oil shale retort wastewater sources and characteristics; (2) identify potentially applicable control technologies capable of treating the identified wastewater streams; and (3) design, construct, and operate pilot-plant facilities to evaluate the selected technologies. This report presents results of Phases I and II, in which literature and other information sources were surveyed to obtain relevant data about oil shale retorting technologies, wastewater sources and characteristics, potential wastewater uses, and potentially applicable treatment technologies. As a result of the study, data gaps were identified, and recommendations for bench-scale treatability studies were made.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Technical Discussion

In-situ retorting, which consists of heating shale underground after modification of the permeability of the rock formation, is being investigated by Dow Chemical Co., Equity Oil Co., Geokinetics, Inc., Occidental Oil Shale, Inc., and Rio Blanco Oil Shale Co., all of which are now conducting process development efforts. Processes being developed by Paraho Development Corp., Superior Oil Co., TOSCO Corp., and Union Oil Co., are classified as surface retorting, in which mined, crushed shale is heated in aboveground metal vessels to produce crude oil. Although many process variations exist within the two major retorting process categories, *in-situ* and surface, distinct wastewater streams are common to most processes within each category. From *in-situ* retorting, three major streams emanate: mine water, retort water, and gas condensate. Mine water is that water pumped from a shale formation prior to ignition. Retort water is formed when water vapor condenses in cool, rubblized shale ahead of the flame front during retorting. Gas condensate is that water which leaves the retort as a gas and is recovered when gas from the *in-situ* retort is cooled.

From surface retorting, three major streams are envisioned: gas condensate, product water, and spent shale pile leachate. Water normally leaves the surface retort in the vapor phase and is recovered as gas condensate when the retort gas is cooled prior to purification. In addition, water separates from the product oil following oil/gas separation and is termed product water.

Since spent shale from surface retorting is to be disposed of above ground, leachate through the shale pile is another potential wastewater stream.

Mine water has been found to exhibit high levels of alkalinity, chemical oxygen demand (COD), chloride, fluoride, sulfate, boron and sodium. Existence of trace metals are of particular concern, since some mine water will be discharged to the environment.

Retort wastewater and product wastewater contain high levels of most pollutants identified. Gas condensate wastewaters exhibit high levels of ammonia, alkalinity, and organics; however, concentrations of trace metals are significantly lower in gas condensate than in retort wastewater. Limited data are available to characterize leachate; however, high levels of organics, total dissolved solids (TDS), sulfate, and sodium have been exhibited.

Water-use schemes developed by industry and government contractors have been reviewed. Most water-use schemes suggest use of wastewater within the retorting facility; however, there appears to be little technical information to support this approach. Available information relating to the treatability of individual retort streams was summarized and significant data were obtained only for the treatability of mine water and combined retort/product water.

In the case of mine water, activated alumina absorption, precipitation with phosphoric acid and lime, and ion exchange have been demonstrated in bench-scale screening tests to remove fluoride and/or boron. Additional technologies should be used for dissolved gas removal, suspended solids removal, TDS removal, and disinfection, particularly if the water is discharged or used for potable needs.

Many research studies have focused on the treatment of retort/product water. There remain, however, key technical questions in the area of emulsified oil separation and organics removal. Steam stripping has been identified as a promising technology for dissolved gases removal. Granular activated carbon and polymeric resins have been demonstrated for gross organics removal; however, for cost considerations, aerobic biological treatment should be the focus for gross organics removal, with carbon and polymeric resins used to remove refractory organics.

No research activity in the area of gas condensate treatment was identified; however, steam stripping should adequately treat gas condensate for inplant use.

In the case of leachate, it is recommended that funds be used to identify leachate as a major wastewater stream and characterize it, rather than investigate treatment alternatives. If leachate is found to be a significant wastewater stream, serious questions regarding leachate collection arise.

Several treatability screening studies have been conducted to fill many treatment step needs identified in Figures 1 and 3, particularly in the case of mine water and retort water treatment. Because of their design and intent, these studies have generally been useful to screen some potential technologies and eliminate others. Many key technical questions still remain unanswered such as:

- How should emulsified oil be separated in retort and product water?
- What is the best system for removal of organics from retort and product water?
- Will state-of-the-art technologies treat gas condensate and leachate?

To answer these questions, and to size pilot-plant equipment, MRC recommends conducting additional bench-scale treatability studies. Presently, there are several opportunities for MRC to obtain relevant samples of retort wastewaters with which to conduct these studies, namely:

- Rio Blanco — mine water and retort water
- Tosco — gas condensate
- Geokinetics — retort water
- Occidental — retort water and gas condensate

In the case of mine water treatment, only Battelle N.W. has conducted bench-scale treatability studies for the removal of fluoride and boron which are of primary concern if the excess mine water is to be discharged or used for potable purposes. Activated alumina absorption and precipitation with phosphoric acid and lime were identified as promising technologies for the removal of boron. The literature reported that electrodialysis and reverse osmosis could produce a more than adequate effluent; however, reverse osmosis appears to be more cost-effective at the high TDS levels expected and has other technical advantages as well.

Thus, additional research is needed to demonstrate the feasibility of reverse osmosis treatment of mine water and to size pilot-plant equipment in the case of other treatment steps.

Suggested technology options to be investigated in these studies are listed in Figure 1.

Many more studies have been conducted with retort water; however, key technical questions remain; e.g., no studies have been conducted to investigate emulsified oil separating from retort and product water. Steam stripping has been identified by several investigators as the best technology for dissolved gases removal, though fouling of column packings has been experienced. Emulsified oil separation may alleviate the problem. Although many studies have been conducted to assess technologies for organics removal, many questions remain. Aerobic biological treatment has classically been the most cost-effective method of organics removal from municipal wastes, but various pretreatments are required for these systems to operate with retort water; also, a large portion of the organics (~50%) appear to be refractory. Therefore, additional studies are needed to identify methods which would enhance the ability of aerobic biological treatment to remove organic compounds. The sensitivity of biological systems to variations in retort water composition has serious implications for commercial operations. If it is found that wastewater cannot be treated biologically, it may become necessary to test physical/chemical methods such as wet air oxidation and granular

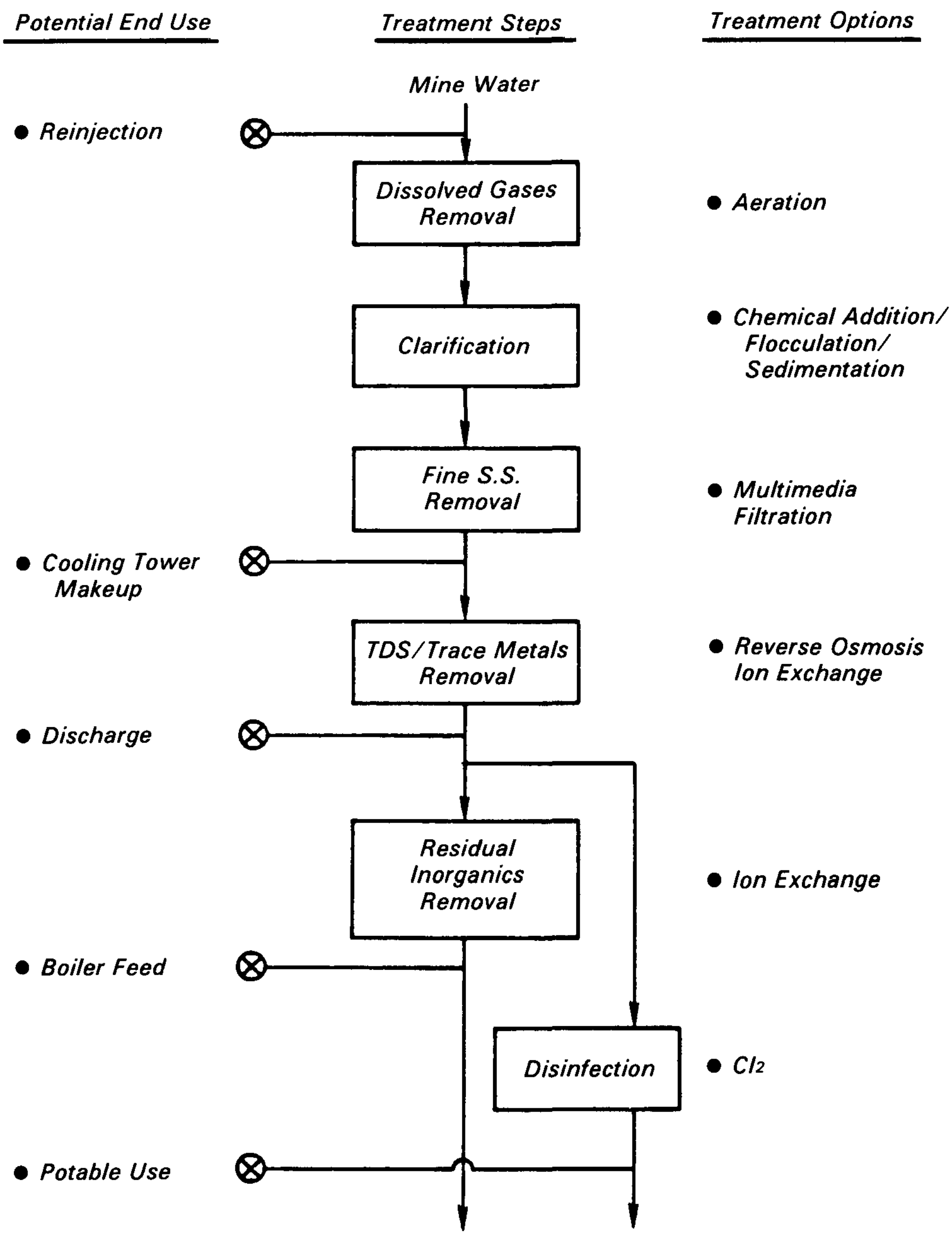

Figure 1. *Mine water treatability options.*

activated carbon adsorption. It is unlikely that retort water would be discharged from a full-scale retorting facility; however, if discharge is necessary, treatment for trace organics, trace metals, and TDS will become necessary. Several investigators have used granular activated carbon and polymeric resins for gross organics removal; however, studies are needed to assess these technologies for their ability to remove refractory organics present in the effluent from the gross organics removal treatment step. Studies of TDS and trace metals removal by reverse osmosis and ion exchange would also become necessary.

Suggested treatment options to treat retort water to discharge quality are shown in Figure 2.

Treatment to discharge quality will probably not be necessary in full-scale systems since many in-plant uses for retort water are envisioned. Bench-scale studies conducted at this time are still recommended to complete a retort treatability data base which would be used by industry and government in making water-use decisions.

Although no known studies exist for the treatment of gas condensate, this stream should not be difficult to treat, compared to retort water. At this time, the extent to which emulsions are present in gas condensate is not known. If present, they will have to be removed prior to subsequent treatment steps. Steam stripping studies are necessary to assess organics removal as well as inorganic dissolved gases removal. If organics remain following steam stripping, studies for their removal will have to be initiated.

Suggested technology options for gas condensate treatment are listed in Figure 3.

Since it is not known whether leachate from spent-shale piles will be present in significant quantities, and leachate quality is still not fully understood, research funds should be directed to address these issues rather than investigating treatment alternatives. If spent-shale piles are found to be porous, and the leachate from percolation through the piles is toxic or unacceptable for groundwater discharge, serious questions about leachate collection in full-scale systems exist.

This report was submitted in partial fulfillment of Contract No. 68-03-2801 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 1979 to March 1980; work was completed as of February 1980.

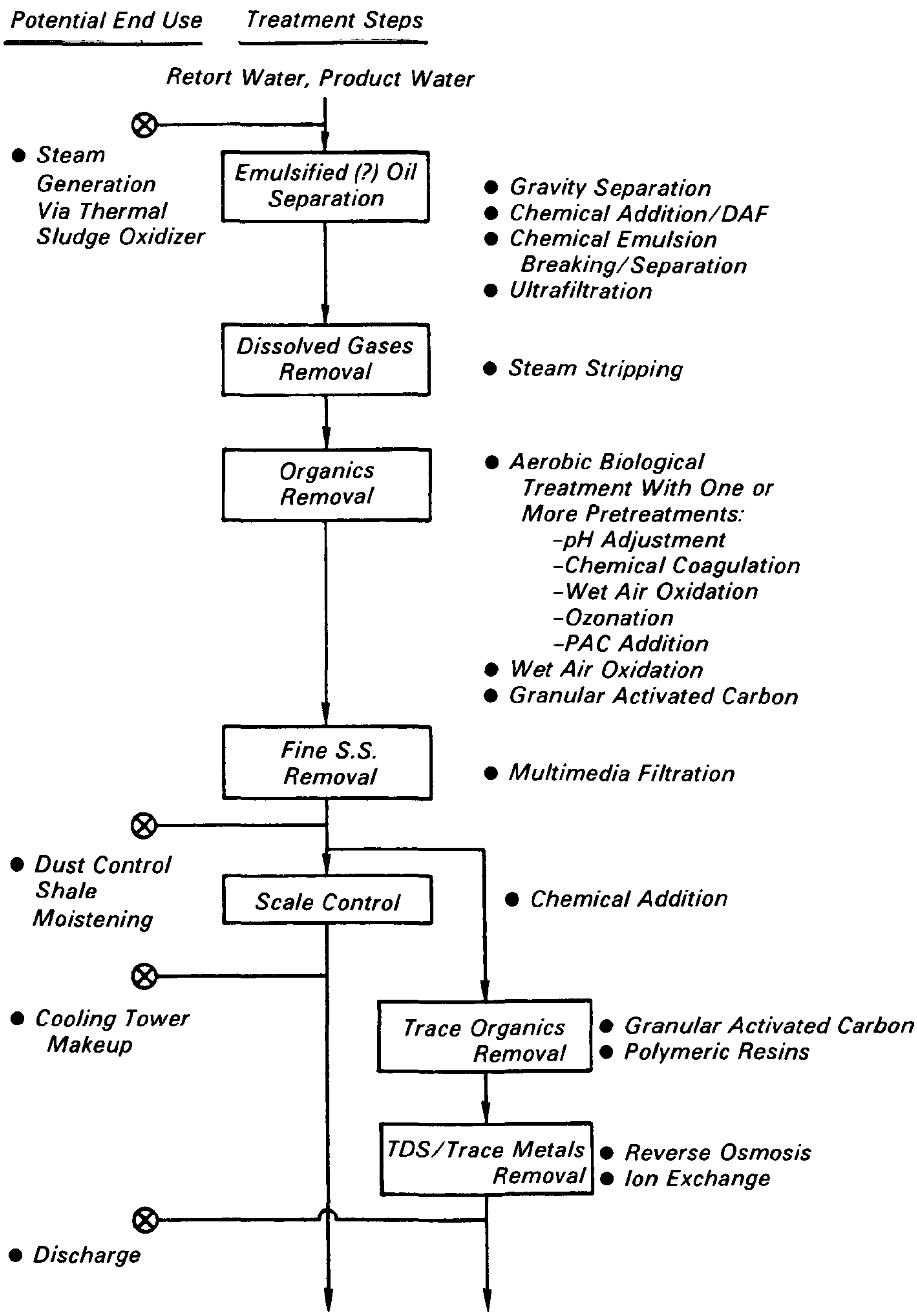

Figure 2. Retort wastewater treatability options.

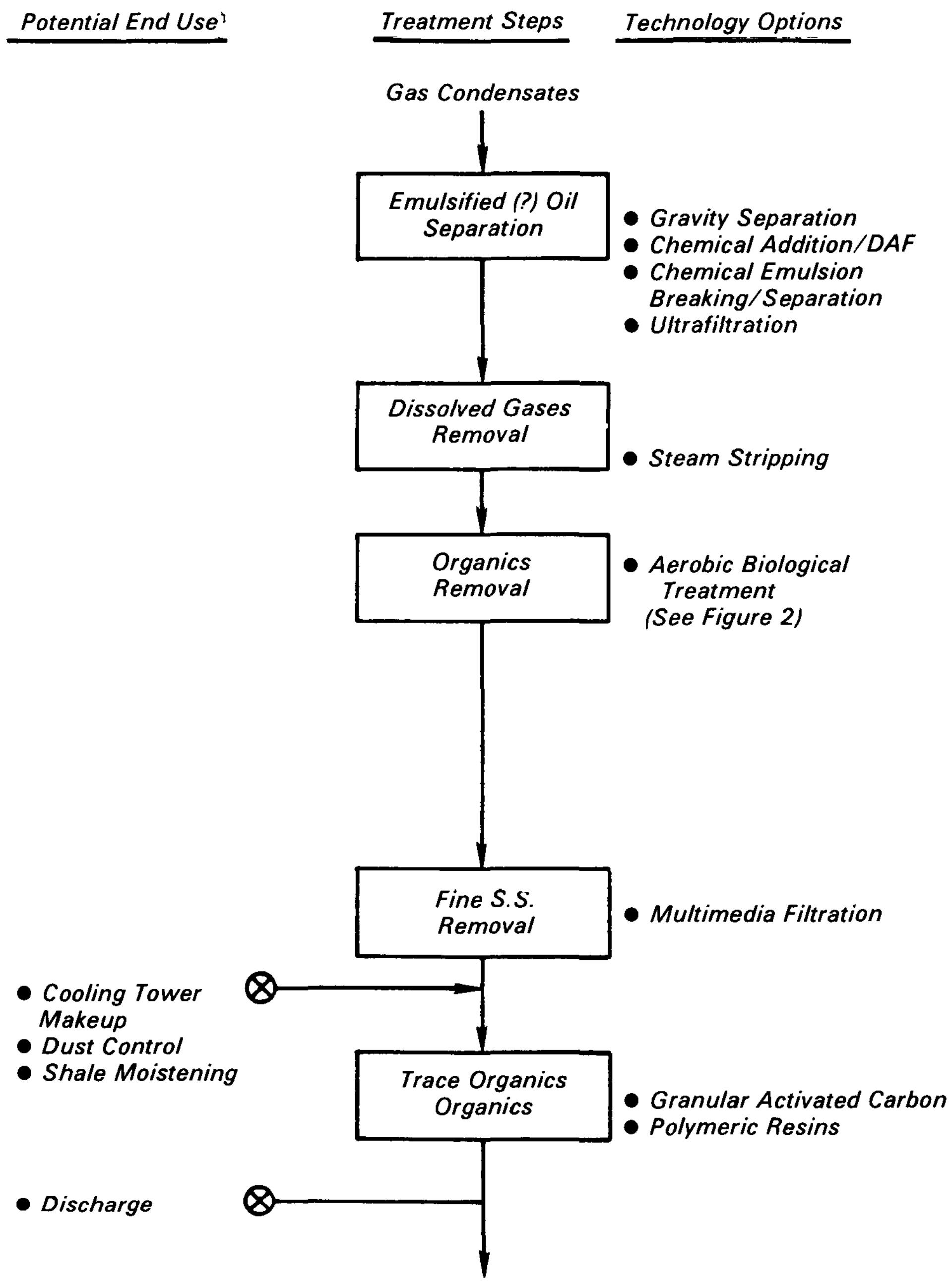

Figure 3. Gas condensate wastewater treatability options.

J. R. Klieve, G. D. Rawlings, and J. R. Hoeflein are with Monsanto Research Corporation, Dayton, OH 45407.
W. W. Liberick, Jr., *is the EPA Project Officer (see below).*
The complete report, entitled "Assessment of Oil Shale Retort Wastewater Treatment and Control Technology—Phases I and II," (Order No. PB 81-187 288; Cost: $9.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

☆ U.S. GOVERNMENT PRINTING OFFICE: 1981 -757-012/7117

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

PS 0000329
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604