**Pressurized Fluidized-Bed Hydroretorting
of Eastern Oil Shales, Volume IV
Task 5 - Operation of PFH on Beneficiated Shale
Task 6 - Environmental Data and Mitigation Analyses
Task 7 - Sample Procurement, Preparation, and Characterization**

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Volume I.

Task 1. PFH Scoping Studies

Task 2. PFH Optimization Studies

Volume II.

Task 3. Testing of Process Improvement Concepts

Volume III.

Task 4. Beneficiation Research

Volume IV.

Task 5. Operation of PFH on Beneficiated Shale

Task 6. Environmental Data and Mitigation Analyses

**Task 7. Sample Procurement, Preparation, and
Characterization**

PROLOGUE

This final report, in four volumes, presents the results of work performed by the Institute of Gas Technology (IGT), during a 3-year research program, September 1, 1987, through May 31, 1991, for the development of a new-generation Eastern oil shale retorting technology, pressurized fluidized-bed hydroretorting (PFH). The research was directed by IGT and was conducted by a research team comprising --

- The University of Alabama's Mineral Resources Institute
- Illinois Institute of Technology
- The Institute of Gas Technology
- The University of Michigan
- The University of Nevada (Reno)
- Ohio State University
- The University of Pittsburgh
- Tennessee Technological University.

The program was managed by the Laramie Project Office of the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) under contract No. DE-AC21-87MC11089.

The Devonian oil shales of the Eastern United States are a significant domestic energy resource. The eventual development of the Eastern oil shale resource is inevitable. It is located in the central portion of the country in close proximity to oil refineries, distribution facilities, and markets. In addition, this resource is located in an area with an established social infrastructure and an available water supply. Most important, although estimates vary, over 400 billion barrels of synthetic liquid fuel may be recoverable from surface-minable shale deposits located in the states of Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee. Furthermore, large surface-minable shale deposits located in the states of Illinois, New York, Pennsylvania, and West Virginia could become viable feedstock for oil recovery when beneficiated.

Over the past decade a number of retorting approaches have been tested for Eastern oil shales; however, the results of these tests show that the highest oil yields are obtained by retorting these shales in the presence of hydrogen at elevated pressures. Oil production from hydrogen-deficient Eastern U.S. oil shales is greatly improved by retorting in a hydrogen atmosphere. Efforts to improve the economics of hydroretorting have led to the development of a second-generation hydroretorting process -- the PFH process at IGT.

The overall objective of this program was to perform the research necessary to develop the new-generation PFH process for retorting Eastern oil shales, incorporating research on technologies in areas such as raw shale

preparation, beneficiation, product separation, and waste utilization and disposal that have the potential to improve the economics of recovering oil from shale using the PFH process.

At the core of the program was the development of a pressurized fluidized-bed hydroretorting process by IGT. IGT obtained data for the development and optimization of the PFH process for both raw and beneficiated shale. IGT also developed PFH data bases for six key Eastern oil shales from Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee.

Researchers at the Illinois Institute of Technology, Ohio State University, Tennessee Technological University (TTU), and the University of Michigan (UM) developed techniques for removing sulfur and nitrogen from shale, evaluated removal of fines from shale oil, evaluated the potential environmental impacts of shale development, and the removal of leachable metals. The University of Alabama's Mineral Resources Institute (MRI) was responsible for the development of more efficient and economical means to beneficiate Eastern oil shales and directed related activities at the University of Pittsburgh. The University of Nevada (Reno) evaluated a novel concept for the comminution of shale using pressure cycling to hydraulically fracture shale.

The program consisted of seven tasks: Task 1. PFH Scoping Studies; Task 2. PFH Optimization Tests; Task 3. Testing of Process Improvement Concepts; Task 4. Beneficiation Research; Task 5. Operation of PFH on Beneficiated Shale; Task 6. Environmental Data and Mitigation Analyses; and Task 7. Sample Procurement, Preparation, and Characterization. An eighth task was devoted to project management and report preparation.

EXECUTIVE SUMMARY

The objective of Task 5 (Operation of PFH on Beneficiated Shale) was to modify the PFH process to facilitate its use for fine-sized, beneficiated Eastern shales. This task was divided into 3 subtasks: Non-Reactive Testing, Reactive Testing, and Data Analysis and Correlations. The objective of the non-reactive testing subtask was to determine operating conditions necessary to achieve the desired residence time of fine shale particles in a fluidized bed (or fluidized in the interstices of a packed bed of inert material). Cold flow testing showed that the small (8 μm) beneficiated oil shale particles formed large (500 to 600 μm) agglomerates. These agglomerates were very soft and could be easily broken up. Beneficiated oil shale was found to fluidize better without using large inert particles in the bed.

The objective of the reactive testing subtask was to conduct a PFH test with beneficiated oil shale. Pelletized beneficiated shale was fed at a rate of about 53 lb/h (24 kg/h) during the test for 3-1/2 hours including a steady-state operation of 1-1/2 hours.

The objective of the data analyses and correlations subtask was to analyze data from various PFH tests and develop a correlation describing the hydroretorting characteristics of beneficiated Eastern oil shales. Test results showed that correlations developed for raw Indiana shale in Subtask 2.4 (Volume I, Final Report) can be used to describe beneficiated Indiana shale conversions; therefore, no separate set of correlations were developed for beneficiated Indiana shale.

The potential environmental impacts of PFH processing of oil shale must be assessed throughout the development program to ensure that the appropriate technologies are in place to mitigate any adverse effects. The overall objectives of Task 6 (Environmental Data and Mitigation Analyses) were to obtain environmental data relating to PFH and shale beneficiation and to analyze the potential environmental impacts of the integrated PFH process. The task was divided into the following four subtasks, which were performed by the indicated program participant: 6.1. Characterization of Processed Shales (IGT), 6.2. Water Availability and Treatment Studies (TTU), 6.3. Heavy Metals Removal (UM), and 6.4. PFH Systems Analysis (TTU and IGT).

Tests were conducted to determine the physical and thermal properties and leaching characteristics of samples of six spent shales that had been hydroretorted in the continuous PFH unit at 600 psig and 900°F (4.2 MPa and 480°C). The physical and thermal properties determined included particle size distribution, permeability, compressibility, compactability, consolidation, shear stress, cohesion, and thermal conductivity. The physical and thermal properties of spent shale affect the design and characteristics of embankments used for storing the material prior to ultimate disposal.

Riffled fractions of each batch of spent shale were agglomerated with oxygen at 2000°F (1095°C) for different times to determine the effects on leachability. Also, a few selected samples were slagged at temperatures in excess of 2500°F (1370°C). The agglomerated and slagged samples, as well as the spent shale samples, were subjected to the EPA Toxicity Characteristic Leaching Procedure (TCLP) to determine if spent shale must be treated as a hazardous material for disposal.

The results showed that the physical properties of spent PFH shales from six states in the Eastern United States differ considerably. The results of shale leaching tests (TCLP) showed that none of the spent shale samples exhibited the toxicity characteristic. In general, thermal agglomeration further reduced the levels of metals leached from the spent shales during TCLP tests.

The objectives of Subtask 6.2 were to assess the availability of water for PFH facilities to process Eastern oil shales and to determine suitable techniques for treating wastewater generated during shale processing. TTU evaluated the sources of free-flowing water courses in the six states involved in the study to determine if sufficient flow were available to supply shale processing plants of different oil production capacities. The proximity of the water course to locations where shale was known to outcrop was also determined. With this information, TTU specified locations in each state at which both sufficient water and shale resources were available to support oil shale processing plants. Restrictions imposed by existing laws and regulations were not considered in this subtask.

TTU also conducted tests in batch and continuous-flow reactors to evaluate the biological treatability of wastewater generated from shale hydroretorting. Because of the limited availability of PFH wastewater from the experimental program, TTU focused their efforts on four compounds demonstrated to be in PFH wastewater: acetone, pyrrole, propionitrile, and sodium thiocyanate. Solutions containing various combinations of these compounds were readily degraded by aerobic treatment at hydraulic retention times of 1 day. The concentration of each compound in the effluent from continuous-flow reactor experiments was less than 1 mg/L.

Activated carbon adsorption or flocculation by ferric chloride or alum were found to be of limited value for primary treatment of the wastewater. However, each could be useful for secondary or polishing treatment.

The objective of Subtask 6.3 was to investigate the catalytic and non-catalytic dissolution of heavy metals from raw and hydroretorted samples of Indiana shale. UM conducted laboratory-scale dissolution tests for iron, barium, cadmium, and chromium using hydrochloric and nitric acids. The dissolution rates could be represented by the power law form of the rate equation over the concentration range of 0.1 to 1.0 M acid. Additions of salt were found to affect the dissolution rates of all elements studied with both rate increases and decreases observed. The results indicated that these effects were not caused by changes in hydrogen ion activity due to salt addition.

Subtask 6.4 consisted of two separate tasks: IGT conducted the work on Subtask 6.4.1 (PFH System Analyses), and TTU conducted the work on Subtask 6.4.2 (Environmental Impact). The objective of Subtask 6.4.1 was to develop a program to define the effluent streams, quantities, and compositions for a PFH plant utilizing various Eastern raw and beneficiated oil shales. An existing computer program written previously by IGT to simulate the moving-bed hydroretorting process was modified and expanded to incorporate the three major components of the PFH process: preheating zone, hydroretorting zone, and cooling zone. As each of these zones in the PFH process is a fluidized bed, the program incorporates coding to calculate the superficial fluidization

velocity for the shale particles, the diameter of the zone to achieve the velocity, and the height of the fluidized bed to achieve a specified residence time. The correlations from the experimental tasks of the project can be incorporated into the computer program for the six shales.

The objective of Subtask 6.4.2 was to provide an environmental assessment of a PFH facility and to compare the results with those from a conventional thermal retorting facility. TTU has determined that the environmental impact of a shale processing plant based on the PFH process will be significantly less than that of a conventional thermal retorting plant. The major impact associated with shale processing is that of excavating, mining, and surface disposal of the processed shale. Because pressurized hydroretorting yields as much as 200% or more oil from the same quantity of shale when compared to thermal retorting, the amount of shale that must be processed and disposed is correspondingly less. Also, TTU summarized the Federal and state laws, rules, and regulations that could impact or affect the development of shale processing facilities in each of the six states involved in the study.

The objective of Task 7 (Sample Procurement, Preparation, and Characterization) was to procure, prepare, and characterize raw and beneficiated bulk samples of Eastern oil shale for all of the experimental tasks in the program. MRI conducted the work on this task.

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INTRODUCTION

The Devonian oil shales of the Eastern United States are a significant domestic energy resource. The overall objective of the 3-year program, initiated in October 1987 by the U.S. Department of Energy (Contract No. DE-AC21-87MC11089), was to perform the research necessary to develop the pressurized fluidized-bed hydroretorting (PFH) process for producing oil from Eastern oil shales. The program also incorporated research on technologies in areas such as raw shale preparation, beneficiation, product separation, and waste disposal that have the potential of improving the economics and/or environmental acceptability of recovering oil from oil shales using the PFH process. The program was divided into eight tasks.

In order to accomplish all the program objectives, the Institute of Gas Technology (IGT), the prime contractor, worked with seven other institutions: the University of Alabama/Mineral Resources Institute (MRI), Illinois Institute of Technology (IIT), the University of Michigan (UM), the University of Nevada (Reno), Ohio State University (OSU), Tennessee Technological University (TTU), and the University of Pittsburgh (UP).

This report (Volume IV) presents the work performed by IGT, TTU, UM, and MRI in Task 5 (Operation of PFH on Beneficiated Shale), Task 6 (Environmental Data and Mitigation Analyses), and Task 7 (Sample Procurement, Preparation, and Characterization) during September 1987 through March 1991.

TASK 5. OPERATION OF PFH ON BENEFICIATED SHALES

The objective of this task was to modify the PFH process to facilitate its use for the fine-size beneficiated Eastern oil shales. This task was divided into three subtasks: Non-Reactive Testing, Reactive Testing, and Data Analyses and Correlations.

Subtask 5.1. Non-Reactive Testing

Objective

The objective of this subtask was to determine operating conditions necessary to achieve the desired residence time of fine shale particles in a fluidized bed (or fluidized in the interstices of a packed bed of inert material).

Technical Discussion

Equipment

The equipment used to conduct the testing in this subtask consisted of a low-temperature test unit and a high-temperature test unit. The low-temperature test unit was used to determine fluidization characteristics of the beneficiated oil shale with various test fluidized beds and at different operating conditions. The high-temperature bed was used to determine the effect of temperature on the fluidization behavior and the amount of entrained solids carry-over from the bed for beneficiated shale.

The low-temperature test unit consisted of a 6-inch- (15.2-cm) diameter Plexiglas column fitted with a porous plate for some tests, or a filter vent type of gas distributor for other tests. The distributor was modified in some tests so that a pulsed-gas distributor could be evaluated. Pressure taps in the lower part of the bed were used to determine the differential pressure across the bed at various operating conditions.

Nitrogen was used as the fluidizing gas and was metered into the bed with a rotameter. The fine solids carried over in the off gas were collected in a cyclone placed at the outlet of the column. All tests in this unit were conducted in the batch mode. A schematic drawing of the fluidization column and distributor (configured for the pulsed-gas tests) is shown in Figure 5-1.

The high-temperature test unit consisted of a 6-inch- (15.2-cm) diameter stainless-steel fluidization column fitted with a bubble-cap type of gas distributor. Six equally spaced bubble caps were located on a circle of 2-inch (5.1-cm) radius from the center of the column. Three 0.0938-inch- (2.4-mm) diameter holes angled downward at 30° were drilled in each bubble cap.

The column was enclosed by an external electric resistance furnace that could heat the system to approximately 1600°F (871°C). Nitrogen was used to fluidize the beneficiated shale in this unit. All tests conducted in this facility were batch tests. A schematic drawing of this facility is shown in Figure 5-2.

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Figure 5-1. EQUIPMENT INSTALLED FOR PULSED FLUIDIZATION TESTS

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Figure 5-2. SCHEMATIC DRAWING OF HIGH-TEMPERATURE FLUIDIZATION TEST UNIT

Material

The material used in the testing was beneficiated Alabama (Chattanooga) oil shale. The results of a standard screen analysis and an analysis from a Coulter Counter are presented in Table 5-1. The sieve analysis indicated an average particle size of about 300 μm . A sub-sieve analysis using a Coulter Counter of a sample that had undergone ultrasonic treatment indicated an average particle size of only 8 μm , with essentially no material larger than 32 μm . The larger apparent particle sizes of the standard screen analysis are a result of the shale's tendency to form soft agglomerates at ambient conditions.

Table 5-1. COMPARISON OF COULTER COUNTER AND STANDARD SCREEN ANALYSIS OF BENEFICIATED ALABAMA SHALE

Coulter Counter

<u>Cumulative Weight Percent Less Than</u>	<u>Diameter, μm</u>
0.0	3.2
9.4	4.0
21.4	5.0
35.8	6.4
51.8	8.0
67.5	10.1
80.4	12.7
89.4	16.0
95.3	20.2
99.4	32.0
100.0	40.3

Standard Screen

<u>Cumulative Weight Percent Less Than</u>	<u>Diameter, μm</u>
4.4	44
29.3	74
33.4	125
39.5	177
45.8	250
56.6	420
78.4	841
99.9	1680

A second batch of beneficiated Alabama shale was obtained for later testing. A particle size analysis of this material is given in Table 5-2. It had a slightly smaller average particle size of 7 μm compared with the first batch of beneficiated shale, but had essentially a very similar size distribution.

Table 5-2. SIZE ANALYSIS OF BENEFICIATED ALABAMA SHALE

Cumulative, wt %	Diameter, μm
0.6	32.0
1.5	25.4
5.0	20.2
11.0	16.0
19.5	12.7
30.5	10.1
42.5	8.0
53.6	6.4
64.0	5.0
73.7	4.0
82.3	3.17
92.0	2.0
96.9	1.26
98.1	1.0
99.7	0.50

D_p (average) - 7.0 μm

Discussion

Beneficiated shale is very small (about 8 μm in average particle diameter). Therefore, one of the objectives of this subtask was to determine if the fine shale could be retained in the bed long enough to react, and not be carried away in the off gas. It was decided to test the beneficiated shale in two ways: with and without large "inert" material in the bed. If the fluidization of the beneficiated shale alone would not be satisfactory, it was hoped that the large inerts would trap the small particles between them and produce long residence times.

In the initial testing a sample of the beneficiated Alabama shale was fluidized with nitrogen in the 6-inch- (15.2-cm) diameter Plexiglas column (without inerts) using a filter vent type of gas distributor, and the bed pressure drops were recorded while the gas velocity was gradually increased. At low gas velocities, the pressure-drop versus gas-velocity curve (Figure 5-3) was typical of fine (Geldart Group C) cohesive materials that tend to channel and expand locally rather than fluidize smoothly. Visual observations made during the test confirmed that gas was channeling through the bed at low velocities. However, at higher gas velocities of about 0.4 ft/s 0.12 m/s, the upper two-thirds of the bed was well fluidized, while material near the wall in the lower part of the bed remained unfluidized.

Two tests were conducted in the 6-inch (15.2-cm) Plexiglas column to determine if different types of gas distributors would improve the fines fluidization near the grid by providing more uniform gas distribution. The first test was conducted with a 3-inch (7.6-cm) layer of 1/4-inch (6.4-mm) glass beads on top of a filter-vent type of distributor. This configuration resulted in more severe channeling at a wider range of gas velocities than the filter-vent distributor alone.

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Figure 5-3. EFFECT OF FLUIDIZATION VELOCITY ON THE PRESSURE DROP ($\Delta P/L$) OF BENEFICIATED OIL SHALE

The second test, conducted with a porous metal distributor plate, yielded better results. At low superficial gas velocities, the resulting fluidization was very similar to that achieved with the filter vents. At higher gas velocities, the quality of fluidization continued to improve until most of the bed was actively fluidized. At a superficial gas velocity of 0.8 ft/s (0.24 m/s), the beneficiated shale fluidized well, and behaved as if its effective particle size was in the range 500 to 600 μm .

The entrainment rate of beneficiated shale was also determined as a function of gas velocity through the bed (without inerts) using the filter-vent gas distributor. The measured entrainment rate at a gas velocity of 0.8 ft/s (0.24 m/s) was less than 0.3% of the entrainable material in the bed. The material collected by the cyclone was all less than 74 μm in size.

Two other tests were conducted in the 6-inch (15.2-cm) Plexiglas column to determine if large-diameter inerts (glass beads larger than 1600 μm) would allow the fines to fluidize within the interstices. The first test was conducted with a 12-inch (30.5-cm) layer of 1/4-inch (6350 μm) glass beads in the column, with beneficiated shale located in a region 2 to 8 inches (5.1 to 20.3 cm) above the distributor. When the gas velocity was increased, both gas and solids channeled up one side of the column, clearing a path for the gas to bypass the rest of the bed. A further increase in fluidizing gas flow rate resulted in increased shale entrainment, while the bed remained static.

A second test was conducted in the Plexiglas column with 16 mm glass spheres and beneficiated shale arranged exactly as described above. However, the shale did not completely fill the voids between the glass spheres as it had previously. The gas velocity was slowly increased to a maximum value of about 1.4 ft/s (0.43 m/s). There was no observed fluidization or movement of shale other than some very minor entrainment of fines. The shale appeared to be trapped between adjacent glass spheres. Based on these and earlier results, it appears that this material will not fluidize satisfactorily within a packed bed of inerts. Therefore, all further testing was conducted with beds of 100% beneficiated shale.

The pulsing of fluidizing gas through beds of very fine materials has been suggested as a means of improving the quality and degree of fluidization at reasonable superficial gas velocities. In order to evaluate this technique with beneficiated oil shale, the equipment required to conduct pulsed-fluidization tests in the 6-inch (15.2-cm) diameter Plexiglas column was installed as previously shown in Figure 5-1. Modifications to the column included a new 19-point gas distributor (Figure 5-4) and the associated fluidizing-gas supply lines.

Shakedown tests of the equipment for pulsed-fluidization tests in the 6-inch (15.2-cm) column were carried out with beneficiated Alabama (Chattanooga) shale. Smooth fluidization and good solids mixing were obtained at lower gas velocities than were previously found with a continuous fluidizing gas flow.,

Pulsed-fluidization tests were then conducted at 24, 40, 60, and 150 pulses/minute over a superficial gas-velocity range of 0.04 to 0.20 ft/s (0.012 to 0.061 m/s). The best fluidization occurred at a superficial gas velocity of 0.2 ft/s (0.061 m/s) and 40 pulses/minute (0.5 s ON/1.0 s OFF).

F881002

Figure 5-4. DIAGRAM OF 19-POINT GAS DISTRIBUTOR
FOR PULSED FLUIDIZATION TESTS

At these conditions, the pulses seemed to lift the shale up off the grid, and the bubbles caused good solids mixing. A gas velocity of approximately 0.6 ft/s (0.18 m/s) was necessary to fluidize the bed equally well with continuous gas flow.

At 24 pulses/minute (0.5 s ON/2.0 s OFF), the bed level would rise as much as 4 inches (10.2 cm) and then fall back again before the next gas pulse occurred. This resulted in intermittent fluidization and little solids mixing. Although fluidization was smoother at 60 pulses/minute (0.5 s ON/0.5 s OFF), a smaller portion of the bed was actively fluidized. Gas bubbles tended to rise up one side of the column, causing a downward flow of solids on the opposite side over the upper two-thirds of the bed.

At 150 pulses/minute (0.2 s ON/0.2 s OFF), some solids segregation occurred between 0.1 and 0.2 ft/s (0.03 to 0.06 m/s) through the bed, but to a lesser extent than with continuous fluidization. The magnitude of the gas pulses was noticeably less than with the other pulse rates, resulting in reduced activity near the distributor at the same gas velocities. A gas velocity of about 0.36 ft/s (0.11 m/s) was required to achieve the same degree of bed mixing that occurred at 0.2 ft/s (0.06 m/s) and 40 pulses/minute.

A fluidization test was conducted with the beneficiated Alabama shale at a temperature of about 530°F (277°C). This test was conducted in the 6-inch (15.2-cm) diameter high-temperature test unit with nitrogen. The purpose of this test was to determine if the beneficiated shale would form soft agglomerates at elevated temperatures like it did at ambient temperature. The design of this unit made it necessary to use purged rather than static pressure taps for the pressure-drop readings. The resulting fluidization curve shown in Figure 5-5, was significantly different from the curve obtained in the Plexiglas column with the original shale sample (Figure 5-3).

The carryover rate of beneficiated shale from the bed was also measured at 500°F (260°C) at gas velocities from 0.3 to 0.8 ft/s (0.09 to 0.24 m/s) in the bed. The results of this test are shown in Figure 5-6, along with the results obtained in the Plexiglas column. To allow direct comparison of test results at low and high [530°F (277°C)] temperatures with the same material in the same equipment, a second entrainment test was conducted.

The fluidization curves obtained at ambient and 530°F (277°C) were very similar, indicating that there was no significant difference in the way this material behaves at the two temperatures. Fines carryover was generally higher at 530°F (277°C) than at 60°F (16°C) over the gas velocity range tested (Figure 5-7). This result suggests that gas viscosity has a greater effect on entrainment than gas density at these conditions.

Beneficiated Shale Feeding Tests

Tests were also conducted to determine a satisfactory way to feed the cohesive oil shale to a fluidized bed. Generally, this type of material bridges in pipes, and does not flow freely.

Initially there was a limited supply of beneficiated shale available; therefore, the first tests were conducted using a fine, cohesive iron oxide material. The tests were conducted using a 1-inch- (2.54-cm) diameter screw

F890101

Figure 5-5. EFFECT OF FLUIDIZATION VELOCITY ON BED PRESSURE DROP ($\Delta P/L$)
 AT ELEVATED TEMPERATURE

F890102

Figure 5-6. EFFECT OF GAS VELOCITY AND TEMPERATURE ON THE ENTRAINMENT RATE OF BENEFICIATED SHALE

F80102A

Figure 5-7. COMPARISON OF BENEFICIATED SHALE ENTRAINMENT RATE AT HIGH AND LOW TEMPERATURES

feeder which passed through a 6-inch- (15.2-cm) diameter feed hopper. An initial problem of fines bridging in the hopper was solved by placing a vibrator on the side of the hopper just above the screw housing. This resulted in a steady flow of fines over a fairly wide range of screw speeds.

Immediately after this testing, about 1,000 pounds (454 kg) of beneficiated Alabama shale was received, and this material was placed in the feed hopper. Although the beneficiated shale feed rate was observed to vary with screw speed, the effective flight loading was not constant, and the feeding technique was deemed unreliable.

In the previous tests, the feed hopper was not fluidized. Therefore, for the next test the hopper was continuously fluidized and a feed test conducted. Although continuous feeding was possible, the feed rate of the shale was not controlled well by the screw speed, and varied as the height of the solids in the feed hopper decreased.

Tulanox, a fumed silica flow conditioner about 0.2 to 1 μm in size, was then added to the beneficiated shale to prevent bridging and channeling in the feed hopper, and to allow constant solids discharge through the screw feeder. Conditioner concentrations of 0.5 to 2 weight percent were tested in the 6-inch- (15.2-cm) diameter feed hopper without success. The negative results were perhaps due to incomplete mixing of the extremely fine powders.

Another beneficiated shale feeding test was conducted in which air was pulsed into the bottom of the 6-inch- (15.2-cm) diameter feed hopper to break up or to prevent bridging of the solids in the feed hopper without actually fluidizing the shale. During the test, the pulse frequency was gradually decreased to 6 times per minute. At pulsing frequencies of 6 to 60 times per minute, the shale flow rate was constant and reproducible. This feeding technique was much more effective than the others tested. A schematic diagram of the equipment used for the pulsing tests is shown in Figure 5-8.

A Plexiglas model of the PFH bench-scale feed hopper was built to test the gas pulsing technique for feeding beneficiated shale in the Bench-Scale PFH Test Program. Initial tests with 2 aeration points along the bottom side of the screw housing were only partially successful. The beneficiated shale could be fed steadily and at a reproducible rate down the center of the hopper, directly above the aeration points. However, shale near the hopper wall was not dislodged by the pulsed gas, and did not flow down to the feed screw. Two more aeration points were added to the model on either side of the feed screw, near the sloped hopper walls. The results of feeding tests were very similar. Only the material directly above the aeration point flowed down to the feed screw. The balance of the material remained in the feed hopper.

Conclusions

1. Cohesive beneficiated Alabama oil shale could be fluidized well at gas velocities above approximately 0.4 ft/s (0.12 m/s).
2. The small (8 μm) beneficiated oil shale particles formed large (500 to 600 μm) agglomerates after fluidizing for a time. These agglomerates were very soft, and could easily be broken up.

F900115

Figure 5-8. SCHEMATIC DIAGRAM OF THE EQUIPMENT USED IN THE PULSE FEEDING TESTS

3. Beneficiated oil shale was found to fluidize better without using large inert particles in the bed.
4. The large agglomerates which formed at ambient temperature, also formed at a temperature of 530°F (277°C).
5. The entrainment rate of beneficiated oil shale from a fluidized bed was greater at high temperature [530°F (277°C)] than at low temperature. This is because the effect of gas viscosity is greater than that of gas density.
6. Fluidizing the beneficiated oil shale using pulsed fluidizing gas was found to be more efficient than using continuous fluidizing air. However, on a commercial unit, the extra equipment required to cause pulsing of the fluidizing gas may not be warranted.
7. Pulsing gas into the feed hopper of beneficiated shale to prevent bridging enabled the beneficiated shale to be fed easily and reliably using a screw feeder.

56WP/61090T5/RPP

Subtask 5.2. Reactive Testing

The objective of this subtask was to conduct PFH tests with beneficiated oil shales in a packed bed of inert solids. The data obtained in Subtask 5.1 was to be used to provide the design for modification of an existing reactor system for achieving the objectives of the subtask.

Discussion

One test was conducted in the bench-scale, advanced multi-purpose research reactor (AMRR) unit with beneficiated Indiana (New Albany) shale. The shale had been pelletized and sized to -20+50 mesh. The results of lab-scale continuous test conducted in Subtask 1.2 with the same material showed the shale particle attrition rate to be low and the carbon conversion for the beneficiated shale to be similar to the carbon conversion of -60+100 mesh raw shale. Pelletized beneficiated shale was used in the AMRR test instead of fines because a preliminary economic calculation showed pelletized beneficiated shale can be more economically retorted in the PFH process.

The beneficiated shale was originally planned to be fed to the bottom of the AMRR and discharged from the top of the reactor. A packed bed of inert solids was to be used as a means of containing good heat and mass transfer. Pelletizing the beneficiated shale allowed the use of the same operational procedure for the pelletized beneficiated shale in the 6-inch (15.2-cm) AMRR as was used for the raw shale. Shale was fed to the top of the fluidized bed with a calibrated screw feeder and discharged from the bottom of the bed through an L valve. No inert solids were added to the reactor.

The AMRR is a highly flexible bench-scale reactor system capable of continuous operation at 1800°F and 1000 psig (982°C and 0.7 MPa). Shale feed rates as high as 100 lb/h (45 kg/h) can be sustained, and the feed hopper is large enough to hold enough shale for a 6 hour test. A schematic diagram of the AMRR, including the reactor, feed hopper, residue receiver, liquid collection system, and environmental sampling train, is presented in Figure 5-9. A more detailed description of the AMRR equipment and test procedures is presented in Subtask 2-3 (Volume I, Final Report).

Test OSAMRR-10 was the last bench-scale test conducted in this program. Unit operation was successful, and shut-down was voluntary after a 90-minute, steady-state period. The length of the steady-state period was chosen to ensure that the cyclone and solids filters did not become filled with elutriated fines. A summary of the operating conditions of Test OSAMRR-10 is presented in Table 5-3. A detailed discussion of the results of Test OSAMRR-10, including yields is presented in Subtask 2.3 (Volume I, Final Report).

FIG 1001A

Figure 5-9. SCHEMATIC DIAGRAM OF THE BENCH-SCALE PFH TEST UNIT

Table 5-3. OPERATING CONDITIONS FOR AMRR TEST WITH
BENEFICIATED SHALE

Test No.	OSAMRR-10
Feed	Beneficiated IN New Albany
Feed Particle Size, mesh	-20+50
Temperature, °F	950
Hydrogen Pressure, psig	1000
Shale Feed Rate, lb/h	52.5
Shale Residence Time, h	0.5
Gas Superficial Velocity, ft/s	0.8
Shale Feed Time, h	3.5
Steady-State Period, h	1.5

56WP/61090T5-2/RPP

Subtask 5.3. Data Analyses and Correlations

The objective of this subtask was to analyze data from various PFH tests and develop correlations describing the hydroretorting characteristics of beneficiated Eastern oil shales fluidized in the interstices of inert solids. Cold-flow, non-reactive modeling data from Subtask 5.1 and reactive data from Subtask 5.2 were to be used in developing the correlations.

Discussion

Correlations have been developed to describe the PFH carbon conversions to oil and gas for the six Eastern shales studied in this program. These correlations, presented in Subtask 2.4, are based on the results of lab-scale batch tests conducted in Subtasks 1.1 and 2.1 and thermobalance tests conducted in Subtask 2.4. Carbon conversions to oil and gas have been described in relation to the temperature, hydrogen pressure, and shale residence time. A complete discussion of the correlations is presented in Subtask 2.4 (Volume I, Final Report), but the organic carbon (C_{Org}) conversion mechanism can be summarized with the following expressions.

$$C_{Org} \longrightarrow C_{Gas} + C_{Oil_1} + C_{Act} + C_{Res_1}$$

$$C_{Act} \longrightarrow C_{Oil_2} + C_{Res_2}$$

where --

$$C_{Oil} = C_{Oil_1} + C_{Oil_2}$$

$$C_{Res} = C_{Res_1} + C_{Res_2}$$

Carbon conversion to gas is a function of temperature, residence time, and shale source. Oil_1 is the oil produced from a shale when no hydrogen is added. The carbon conversion to active carbon is a function of hydrogen pressure and shale source. The split of active carbon between oil and residue is a function of temperature and shale source. The generation of Oil_2 is also a function of shale residence time.

PFH tests have been conducted in this project with both raw and beneficiated Indiana New Albany shale at similar conditions in various units. The beneficiated shale was pelletized, without binders, before retorting. This was a change from the original work plan in which beneficiated shale fines were to be tested. The shale was pelletized because preliminary economic calculations indicated that PFH processing of pelletized, beneficiated shale has more favorable economics than PFH of raw shale.

A comparison of the test conditions and carbon conversions for similar raw and beneficiated shale PFH tests is presented in Table 5-4. A review of the comparable tests in various process units shows that carbon conversions to oil and gas are similar for the raw and beneficiated shale. Changes in temperature and hydrogen pressure have similar effects on the carbon conversions of the two shales.

Table 5-4. CARBON CONVERSIONS FROM TESTS WITH RAW AND BENEFICIATED INDIANA SHALE

Test	Unit	Shale	Temperature, °F	H ₂ Pressure, psig	Residence Time, min	Carbon Conversion, %		
						to Oil	to Gas	Total
TB-90-17	TB ¹	Raw	950	600	30	NA	NA	66
TB-90-13	TB	Ben.	950	600	30	NA	NA	73
84	Batch ²	Raw	913	600	20	57	16	73
95	Batch	Raw	936	600	20	62	13	75
110	Batch	Raw	945	600	20	62	14	76
96	Batch	Ben.	912	600	20	62	14	76
45	Batch	Raw	914	1000	20	71	15	84
35	Batch	Raw	952	1000	20	72	14	86
38	Batch	Raw	1012	1000	20	69	20	89
120	Batch	Ben.	957	1000	20	69	15	84
C-53	Cont. ³	Raw	916	600	12	49	18	67
C-55	Cont.	Ben.	916	600	15	51	17	68

¹ Thermobalance.

² Lab-scale batch unit.

³ Lab-scale continuous unit.

NA = Not available.

Tests TB-90-17 and TB-90-13 were conducted at similar conditions in the thermobalance with raw and beneficiated Indiana shales. The test conditions were chosen to allow a comparison to be made between the weight loss rates for the two shales. A comparison of the normalized weight loss in percent of the total weight loss as a function of time is shown in Figure 5-10. Weight loss traces can be interpreted in terms of organic carbon conversions by means of a simple correlation. The figure shows the rate of weight loss is similar for the raw and beneficiated shales. Beneficiation of Indiana shale does not appear to change the rate of organic carbon conversion to gas or oil.

Test results summarized in Table 5-4 and Figure 5-10 show that the organic carbon conversion correlations developed for Indiana shale can also be used to describe beneficiated Indiana shale organic carbon conversions. Therefore, no separate set of organic carbon conversion constants were developed for the beneficiated Indiana shale.

56WP/61090T5-3/RPP

Figure 5-10. NORMALIZED RAW AND BENEFICIATED SHALE WEIGHT LOSSES AT 950°F AND 600 psig IN THE THERMOBALANCE

TASK 6. ENVIRONMENTAL DATA AND MITIGATION ANALYSES

Overall Task Objectives

The overall objectives of this task were to obtain environmental data relating to PFH and to shale beneficiation and to analyze the potential environmental impact of the integrated PFH process.

Subtask 6.1. Characterization of Processed Shales

Objectives

Specific objectives of Subtask 6.1 (conducted by IGT) were to determine the physical and chemical properties of oil shales from six Eastern states that had been retorted by the PFH process. The task was conducted from September 1987 to March 1991.

Background

As engineers and scientists developing advanced energy technologies, our responsibilities include ensuring that large-scale, commercial development of an industry based on producing oil from shale is environmentally sound. The steps required to process shale in above-ground retorting facilities include excavation and mining, feedstock preparation, thermal processing, spent-shale conditioning for disposal, ultimate disposal, and land reclamation. The quantities of shale (from either the Eastern or Western U.S.) that must be excavated and processed to yield the necessary oil can be substantial. For example, to produce 50,000 barrel/day of oil, a conventional thermal retorting plant would require as much as 210,000 ton/day of shale (for example, Eastern shale with a Fischer Assay of 10 gal/ton). The plant would produce 178,500 tons of spent shale each day. Over the 20-year operating life of the plant, nearly 1.18×10^9 tons of spent shale would be generated and require disposal in an environmentally acceptable manner. A similar-sized plant based on PFH technology would require 105,000 ton/day of Eastern shale, produce 89,250 ton/day of spent shale, and accumulate 0.59×10^9 tons of spent shale over the 20-year plant operating life.¹ According to Tolbert *et al.* the major environmental impact associated with shale processing is that of surface disposal of the spent shale.²

It is generally known that during the mining and retorting processes, shale increases in volume from its original *in-situ* size. Typically, the increased volume is about 20% greater^{3,4} than that of the *in-situ* raw shale. A study by Oak Ridge National Laboratory (ORNL) indicates that the volume of spent shale could be as much as 85% greater than its *in-situ* volume, depending upon the extent of post-retorting processing (which could include roasting and minerals recovery operations).⁵ Calculations by ORNL further suggest that only 50% to 55% of the spent shale could be backfilled into the mine without some form of compaction, leaving a substantial amount that must be disposed of in surface or landfills.⁵

Physical Properties

The physical properties of the spent shale determine the geometry and size of an embankment in which the spent shale will be stored. The angle of

internal friction provides the maximum slope for the sides of the embankment to prevent sliding failure. The compactability and compressibility of the spent shale relate to the volume occupied by the shale at the optimum moisture content. The relative flow of water through the pile, which may affect leaching of environmentally sensitive (priority) metals, is related to the permeability or hydraulic conductivity. Thermal conductivity affects the rate at which hot shale from the retort will cool to temperatures appropriate for moisturization and disposal.

Numerous studies have been conducted to determine the physical properties of raw and spent shales that affect the structural and environmental stability of embankments designed for storage. Drnevich *et al.* evaluated the moisture-density relationship, permeability, triaxial compression strength, and Atterberg limits of samples of retorted and hydroretorted (HYTORT) shales from Kentucky (among other shales and tests).^{6,7} Heat capacity and thermal conductivity were determined for core samples of Kentucky (Cleveland and Huron) shale up to 200°C by Gilliam.⁸ Mechanical and thermal properties were determined for pieces of Western shale for *in-situ* processing.^{9,10} McWhorter found that the hydraulic conductivity of combusted Western shales decreased significantly over time as a result of hydration.^{11,12}

Based on results of these and other investigations, several embankment designs have been proposed for spent Eastern and Western shales.^{3,6,13-15}

Chemical Properties

The chemical properties of shale determined during this project relate specifically to the leaching of raw and spent shale by precipitation in storage piles. Raw shale will be exposed to weather during storage in stockpiles prior to processing. After processing, spent shale will also be exposed to weather in stockpiles prior to ultimate disposal. It is during these exposures that the most significant environmental impacts could be realized by the leaching of trace metals (in addition to other components) into water in the shale. The test used to evaluate the leaching characteristics of shale samples is the TCLP (Toxicity Characteristic Leaching Procedure), promulgated by the U.S. Environmental Protection Agency (EPA) in 1990.¹⁶

If the concentration of any trace element in the leachate from the TCLP test with shale exceeds Federal limits (Table 6-1), the material is classified as hazardous and must be disposed of in suitably constructed and monitored landfills. If the leachate is not effectively contained or collected, it could percolate down to the water table or combine with surface runoff to contaminate fresh water supplies. The sulfur content of the shale affects its leachability. A shale high in sulfur will yield leachate that is more acidic.

Thermal processing reduces the concentration of acid-forming components in shale, and yields leachate that is less acidic. Other elements of importance, such as nickel and thallium (and molybdenum), have been considered for inclusion on the list of priority metals. Regulations promulgated by the EPA in the future may include these elements as well as others determined to pose significant environmental threats.

Table 6-1. EPA TCLP LIMITS FOR METALS¹⁶

<u>Element</u>	<u>TCLP Leachate Limit, mg/L</u>
As	5
Ba	100
Cd	1
Cr	5
Pb	5
Hg	0.2
Se	1
Ag	5

The leaching characteristics of raw and spent shales from both the Eastern and Western United States have been the subject of numerous investigations ranging from laboratory extractions^{17,18} to long-term lysimeter testing.¹⁹ A large-scale environmental chamber capable of simulating natural rainfall under carefully monitored conditions has recently been constructed and tested with combusted Western shale by the University of Wyoming.²⁰ Theoretical studies have been conducted to model the spent shale system based on thermodynamic properties.²¹

The objectives of these studies and tests have been to quantify and evaluate the effects of "weather" on piles of spent shale so that the environmental impact of this facet of oil shale processing could be predicted. According to Robl,¹⁹ the EPA TCLP or ASTM (American Society for Testing and Materials) leaching methods have little predictive value. Sullivan²¹ suggests that a humidity cell is a much better indicator of trace element release than the TCLP. Sullivan also indicates that the greatest hazard associated with trace element release is with raw shales and least with combusted shales. Sullivan detected no soluble organic compounds in acid or TCLP leachates.²

Gilliam *et al.*¹⁷ described a significant decrease in the acid leachability of trace elements from shales that had been roasted in air at temperatures exceeding about 1382° to 1562°F (750° to 850°C). He attributed this to the phase change or sintering that the sample experienced at these temperatures.

Equipment and Experimental Procedures

Shale Samples and Preparation

Samples of shale for the physical and chemical properties tests were hydroretorted in the continuous PFH unit at a temperature of 900°F (482°C) in hydrogen at a pressure of 600 psig (4.2 MPa) for residence times ranging from 20 to 30 minutes. Details of the PFH process development equipment and procedures have been described elsewhere.²² The particles size consist of the raw feed shale ranged from -40+60 to -60+100 mesh. The samples included spent PFH shale samples from Indiana and Kentucky (New Albany), Ohio (Cleveland),

Alabama and Tennessee (Chattanooga), and Michigan (Antrim). The physical and chemical properties of a sample of raw Indiana shale were also determined for comparison. Spent shale samples from continuous PFH Tests C-1 and C-20 were tested to determine variability in the results. Test C-1 was conducted at a higher average temperature [about 1000°F (538°C)] and residence time (about 150 minutes) than Test C-20, which was conducted at the conditions described above.

The physical properties tests were conducted by the Illinois Institute of Technology (IIT) Department of Civil Engineering. When the tests were completed, the samples were returned to IGT and each was riffled into 3 fractions. The samples in the first fraction were subjected to the TCLP. Those in the second fraction were agglomerated in a laboratory-scale fluidized-bed reactor at 2000°F (1093°C) and then subjected to the TCLP (the agglomeration process is described below). A sample of the Indiana shale and the Michigan shale were slagged in a laboratory furnace and then subjected to the TCLP. The objective of these tests was to determine the effects of processing severity on the leaching characteristics of the spent PFH shale samples.

During agglomeration, the particles in a fluidized bed are heated to near their softening temperature. Under specific hydrodynamic conditions, the particles stick together and grow in size by accretion. When the particles become large enough, the fluidizing gas can no longer support them and they can be removed from the reactor by gravity. In uncontrolled agglomeration, the particles can combine into a single, undesirable sinter. The use of agglomeration for removing high-ash content pellets from a reactor is integral to IGT's U-GAS coal gasification technology. Extraction procedure toxicity tests (the forerunner to the TCLP) have shown that the agglomerated pellets of coal ash from the U-GAS process are essentially nonleachable and, therefore, environmentally innocuous.

The 2-inch (5.1-cm) diameter, laboratory-scale batch unit used to agglomerate the spent shale samples is shown schematically in Figure 6-1. Prior to the test, a weighed amount (about 150 grams) of shale was charged to the reactor. During heat up, nitrogen was fed to the reactor grid and central jet at 4 SCFH (113 L/h) each -- sufficient to maintain a fluidized bed. When the target temperature of 2000°F (1093°C) was achieved, the nitrogen flow to the central jet was replaced by air at 4 SCFH (113 L/h). The oxygen content of the total gas to the reactor was about 10 mole percent.

Tests were conducted with each sample of spent shale to achieve 3 different levels of carbon combustion. The test duration was calculated to ensure that about 1.5, 1.0, and 0.5 times the stoichiometric amount of oxygen required to completely oxidize the carbon (plus sulfur) present in the shale was fed to the reactor. The product from each of the agglomeration tests consisted of a sinter and unincorporated fines [-1/8 inch (3.2 mm)]. The sinter typically comprised 50% to 75% of the feed shale weight and its size was proportional to combustion time. A blank test was conducted with no air fed to the reactor to determine if temperature alone could generate agglomerates -- none were formed. A total of 19 tests were conducted in the batch fluidized bed unit with spent shales.

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Figure 6-1. SCHEMATIC DIAGRAM OF THE FLUIDIZED-BED SHALE AGGLOMERATION UNIT

The samples of slagged shale were prepared in an existing penetrometer viscometer used to determine the viscosities of coal slags. The essential elements of the penetrometer viscometer (Figure 6-2) are a furnace to maintain the temperature of the slag sample within the crucible, a weighted needle with a variable counterbalance to exert a predetermined weight on the needle and a linear variable transducer to measure both the depth and rate of penetration. The complete penetrometer viscometer has four major reactor subsections: furnace system, tower-measurement apparatus, sample preparation-delivery assembly, and gas-purging system.

The Kanthal Corporation EPD fast-heat-up high-temperature melting furnace was selected for the main reactor. Temperatures of about 3000°F (1649°C) can be achieved within 8 minutes, with a guaranteed uniform temperature of $\pm 3^\circ\text{F}$ ($\pm 1.7^\circ\text{C}$). One modification that has been made to segregate the reactor gases from the heater surfaces is the addition of a continuous ceramic reactor core with appropriate seals.

The counterbalanced tower-measurement assembly uses an extremely accurate LVDT to measure the sample penetration depths. A precision drill chuck holds the ceramic penetrometer probe with its metal tip above the sample. The entire assembly is horizontally adjustable in two directions to ensure centerline accuracy.

The insertion and removal of the sample is accomplished with a hydraulic lift mechanism. The smooth, fluidic movement of the apparatus ensures the stable but quick removal of the sample for quenching.

Finally, the gas-purge system to the penetrometer is controlled by a precision Brooks mass-flow controller. All flow commands are remotely made from the control panel board. The board also controls the furnaces and power, and records the LVDT output. An x-y recorder is used to record the penetration depth versus time. The slope of this curve gives the rate of penetration.

The objective of the two tests with Tennessee shale was to determine if the slagging atmosphere (air or nitrogen) affected subsequent leaching characteristics. The objective of the test with Michigan shale was to determine leaching characteristics for comparison with spent Tennessee shale. The first sample of spent Tennessee shale was slagged in nitrogen at 2500°F (1371°C); the second in air also at 2500°F (1271°C). The sample of spent Michigan shale was slagged at 2700°F (1482°C). To prevent contamination of the slagged sample by the crucible material, the samples were contained in ceramic boats.

Physical Properties

The physical properties of the samples of raw and spent PFH shales were determined using ASTM standards or laboratory procedures developed by the IIT Civil Engineering Department. The tests and procedures, listed in Table 6-2, were conducted in the indicated order to minimize the impact on subsequent tests.

Figure 6-2. SCHEMATIC DIAGRAM OF THE PENETROMETER VISCOMETER
USED FOR PREPARING THE SAMPLES OF SLAGGED SPENT SHALES

**Table 6-2. PHYSICAL PROPERTY TESTS AND SEQUENCE
USED FOR RAW AND PFH PROCESSED SHALE SAMPLES**

<u>Sequence</u>	<u>Physical Property</u>	<u>Test/ASTM Standard</u>
1	Particle Size	D 492
2	Thermal Conductivity	IIT Laboratory Test
3	Permeability	D 2434-74 (Falling Head)
4	Consolidation/ Compressibility	D 2435-80
5	Shear Strength/ Triaxial Compression	IIT Laboratory Test
6	Compactability	D 698-78 (Harvard miniature)

Chemical Properties

The toxic or non-toxic character of a solid sample is determined by subjecting it to the TCLP (EPA Method 1311). In the TCLP, the solid sample is mixed with 20 times its weight of an appropriate aqueous extraction fluid (depending upon alkalinity) for 18 hours. After the extraction, the concentration of metals (listed in Table 6-1) in the leachate (plus volatile and nonvolatile organic compounds) are determined. If the concentration of any metal (or organic compound) in the leachate exceeds the regulatory limit, the material is said to exhibit a toxic character and is classified as a hazardous waste. The solid must then be disposed of in suitably constructed and monitored landfills. Because this task focused on the heavy metals in shale, the leachate was not analyzed for organic compounds.

TCLP tests were conducted with raw Indiana and spent shale samples both "as received" and after thermal treatment (agglomeration and slagging). Because of limited sample availability, the TCLP procedure was modified somewhat by proportionately reducing the quantities of shale and extraction fluid. If the results of TCLP tests on "as received" and agglomerated spent shales are similar, the spent shale could be disposed of without further processing.

Discussion of Results

Physical Properties

Overall, the physical properties of samples of raw Indiana and spent PFH shales showed considerable variability. The results of thermal conductivity (TC), permeability, consolidation (compressibility), shear strength, and compactability tests are presented in Tables 6-3, 6-4, and 6-5. The particle size distributions of the raw and spent samples of shale before any physical tests were conducted are presented in Table 6-6.

Table 6-3. RESULTS OF THERMAL CONDUCTIVITY AND PERMEABILITY TESTS CONDUCTED
ON SAMPLES OF RAW INDIANA AND SPENT SHALES FROM SIX STATES

Shale Test No.	IN(NA)		KY(NA)		OH(CL)		AL(CH)		TN(CH)		MI(AN)	
	Raw	C-1	C-20	C-15	C-16	C-14	C-17	C-28	C-17	C-28	C-17	C-28
Thermal Conductivity, W/m-K (Btu/h-ft-°F)	0.27 (0.16)	0.27 (0.16)	0.63 (0.36)	0.41 (0.24)	0.80 (0.46)	0.21 (0.12)	1.13 (0.65)	1.01 (0.58)	1.13 (0.65)	1.01 (0.58)	1.13 (0.65)	1.01 (0.58)
At Density, g/cm ³	1.16	1.10	1.06	1.19	1.11	1.10	1.25	1.28	1.25	1.28	1.25	1.28
Permeability, cm/s	1.25E-3	1.46E-3	7.69E-4	1.22E-2	9.46E-3	1.34E-2	1.99E-3	7.65E-4	1.99E-3	7.65E-4	1.99E-3	7.65E-4
k ₂₀	1.04	0.98	0.98	0.90	1.06	0.92	0.87	1.16	0.87	1.16	0.87	1.16
At Density, g/cm ³												

Table 6-4. RESULTS OF CONSOLIDATION AND SHEAR STRENGTH TESTS CONDUCTED
ON SAMPLES OF RAW INDIANA AND SPENT SHALES FROM SIX STATES

Shale Test No.	IN(NA)		KY(NA)		OH(CL)		AL(CH)		TN(CH)		MI(AN)	
	Raw	C-1	C-20	C-15	C-16	C-14	C-17	C-28	C-17	C-28	C-17	C-28
Consolidation												
Void Ratio, Vol. Void/Vol. Solid												
Initial	1.37	1.76	1.67	1.65	1.60	1.85	2.23	1.27	2.23	1.27	2.23	1.27
Final	0.61	0.50	0.47	0.52	0.48	0.68	0.69	0.38	0.69	0.38	0.69	0.38
Density, g/cm ³												
Initial	1.12	0.98	0.98	0.98	1.00	0.91	0.81	1.14	0.81	1.14	0.81	1.14
Final	1.65	1.77	1.78	1.71	1.76	1.55	1.54	1.88	1.54	1.88	1.54	1.88
Consolidation Factors												
C _c	0.033	0.037	0.02	0.023	0.022	0.024	0.026	0.030	0.026	0.030	0.026	0.030
C _c	0.53	0.85	0.7	0.47	0.51	0.46	0.43	0.475	0.43	0.475	0.43	0.475
Shear Strength												
Angle of Internal Friction, °	36.3	37.6	27.5	40.5	24.4	40.9	33.2	30.3	33.2	30.3	33.2	30.3
Cohesion (c), kPa (psi)	2.8 (0.4)	0.0 (0.0)	22.5 (3.3)	1.4 (0.2)	27.6 (4.0)	0.0 (0.0)	13.8 (2.0)	13.8 (2.0)	13.8 (2.0)	13.8 (2.0)	13.8 (2.0)	13.8 (2.0)
At Density, g/cm ³	1.14	1.20	1.10	1.21	1.21	1.23	1.23	1.20	1.23	1.20	1.23	1.20

Table 6-5. RESULTS OF COMPACTABILITY TESTS CONDUCTED ON SAMPLES OF RAW INDIANA AND SPENT SHALES FROM SIX STATES

Shale Test No.	IN(NA)		KY(NA) C-15	OH(CL) C-16	TN(CH) C-17	AL(CH) C-14	MI(AN) C-28
	Raw	C-1					
Compaction Test Results (Harvard Miniature)							
Optimum Moisture Content (OMC), wt %	20.0	20.0	24.0	22.0	24.0	22.0	22.5
Maximum Dry Density (MDD), g/cm ³	1.50	1.35	1.40	1.43	1.44	1.36	1.55
Particle Size Distribution, wt %							
+40	0.2	--	0.1	0.3	--	--	--
-40+50	4.6	1.2	7.9	23.3	5.0	0.6	--
-50+70	27.0	10.0	29.4	33.9	7.9	8.6	8.2
-70+100	34.7	27.4	15.7	11.4	21.3	23.8	27.6
-100+170	19.0	28.3	11.1	10.4	24.8	17.8	23.7
-170+200	3.5	5.2	3.5	2.6	4.2	3.3	5.8
-200+Pan	11.0	27.9	32.3	18.1	36.8	45.9	34.7
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 6-6. PARTICLE SIZE DISTRIBUTION OF THE SAMPLES OF RAW AND SPENT SHALES FOR PHYSICAL PROPERTIES TESTS

Shale Test No. Sample Weight, g	Indiana		Alabama		Kentucky		Ohio		Tennessee	
	Raw	C-1	C-14	C-15	C-16	C-17	C-16	C-17	C-16	C-17
Particle Size Distribution										
+40	0.00	--	0.02	0.00	1.58	0.07	--	--	--	--
-40+50	0.03	0.00	--	19.48	--	--	--	--	--	--
-50+60	0.25	0.07	--	--	79.92	2.16	--	--	--	--
-40+70	--	--	--	60.34	--	--	--	--	--	--
-50+70	--	--	--	--	--	--	--	--	--	--
-60+70	22.49	9.75	--	--	--	--	--	--	--	--
-40+100	--	--	75.07	--	--	--	--	--	--	--
-70+100	41.08	38.04	--	14.55	11.95	36.30	--	--	--	--
-100+120	--	--	15.29	--	1.51	18.53	--	--	--	--
-100+140	--	--	--	2.58	--	--	--	--	--	--
-120+140	--	--	2.91	--	0.85	12.01	--	--	--	--
-100+200	30.42	--	--	--	--	--	--	--	--	--
-140+200	--	7.79	2.06	0.05	0.91	9.63	--	--	--	--
-200+Pan	5.73	9.52	4.65	3.00	3.28	21.30	--	--	--	--
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The highest value for TC (1.13 W/m-K) was observed for Tennessee shale; the lowest (0.21 W/m-K) for Alabama shale -- both from the Chattanooga formation. TC was 0.27 W/m-K for the raw Indiana shale sample and 0.27 and 0.63 W/m-K, respectively, for the spent Indiana shale samples (C-1 and C-20). The TC of core samples of Kentucky shale was determined to be 0.95 W/m-K by Gilliam.⁸ The TC of Western shale pieces ranged from 0.5 to 1.7 W/m-K, depending upon shale grade.¹⁰

The permeability (k_{20}) of Indiana shale decreased with PFH processing from 1.25×10^{-3} (raw) to 1.46×10^{-3} and 7.69×10^{-4} cm/s. The k_{20} (permeability corrected to 20°C) of the other shales tested ranged from 1.22×10^{-2} to 1.99×10^{-3} cm/s. Drnevich⁶ found the permeabilities of other thermally treated Eastern shale samples to be in the range of 10^{-3} to 10^{-4} cm/s. The permeabilities of retorted Western shale samples were in the range of 10^{-4} to 10^{-5} cm/s.²³ Permeabilities of treated Western shales decrease significantly due to hydration and cementation reactions.¹¹

The results of consolidation tests showed that hydrotorting did not significantly affect the compactability of spent shales. The compacted bulk density of spent shales ranged from about 1.54 to 1.88 g/cm³ (96.1 to 117.1 lb/ft³); that of raw Indiana shale was 1.65 g/cm³ (103.0 lb/ft³). The factors, C_c' and C_c , are obtained from the consolidation tests. C_c' is an indication of the rebound (springiness) of the sample during consolidation -- a higher value for C_c' indicates a higher rebound. C_c is a measure of the rate at which the sample will consolidate. A sample with a high C_c will consolidate at a faster rate than one with a low value of C_c .

The angle of internal friction was determined to be 36.3° for raw Indiana shale and 27.5° and 37.6° for the two spent PFH Indiana shale samples. The angle of internal friction for the other spent shale samples ranged from 24.4° to 40.9°. The cohesion (c) of the samples was 2.8 kPa (0.4 psi) for raw Indiana shale, and 0.0 and 22.5 kPa (0.0 and 3.3 psi) for the two spent Indiana samples, and ranged from 0.0 to 27.6 kPa (0.0 to 4.0 psi) for the samples of spent shales. According to Drnevich,⁶ the angle of internal friction ranged from 22° to 45° and cohesive strengths from 0.0 to 15.2 kPa (0.0 to 2.2 psi) for samples of Kentucky shales.

Because of the limited sample quantities available, tests to determine compactability were conducted using a Harvard miniature mold. The Harvard miniature mold has a 3.3-cm diameter, a height of 7.15 cm, and a capacity of 61.15 cm³. The standard mold for this procedure has a diameter of 10.16 cm, a height of 11.64 cm, and a capacity of 944 cm³. The optimum moisture content (OMC) for all samples ranged from 20 to 24% of the dry sample weight. Maximum dry densities (MDD) ranged from 1.3 to 1.55 g/cm³ (81.1 to 96.7 lb/ft³). Samples of raw, retorted, and hydrotorted (HYTORT) Kentucky shale [-3/4 inch (-19.1 mm)] had OMCs of 12.6, 11.3, and 29.1%, respectively.⁶ MDD were 1.61, 1.38, and 1.27 g/cm³ (100.3, 86.4, and 79.1 lb/ft³), respectively.⁶

The compactability tests yielded significant increases in the -200 mesh fraction of the shale samples tested, compared to the feed material. Compaction increased the -200 mesh component of the raw Indiana shale from 5.7 to 11.0%. Hydrotorting increased the -200 mesh component of Indiana shale from 9.5 and 7.3 to 27.9 and 40.8%, respectively. Thus, the spent shales are more friable than the raw shale tested.

Chemical Properties

The results of TCLP tests conducted on samples of raw Indiana and spent PFH shales, and on spent shales that had been agglomerated/combusted for 0.5, 1.0, and 1.5 hours are presented in Tables 6-7, 6-8, 6-9, and 6-10, respectively. The results of TCLP tests conducted on selected samples of spent Tennessee and Michigan shales that were slagged in the penetrometer viscometer are presented in Table 6-11. The results show that none of the regulatory limits for leachate concentration were exceeded by any of the samples. More importantly, the levels of the priority trace elements in the leachate are at least 1/10th the TCLP limit. The concentration of Cd approaches the TCLP limit of 1 mg/L for the spent PFH shale from Ohio (0.27 mg/L). Slagging further reduced the leachability of the Tennessee and Michigan spent shales.

Figures 6-3 through 6-9 compare the ratio of the concentration of each priority element in the shale leachate to the TCLP limit. (If the concentration of the element was less than the analytical detection limit, the detection limit was used in preparing the figure.) Figure 6-3 shows that for Indiana shale, the ratios are all less than 0.1. In general, except for arsenic, the raw Indiana shale sample was leached to a greater extent than the spent PFH shale.

Figures 6-4 through 6-9 show the effect of processing severity on the TCLP results for shale samples that were first hydroretorted (PFH) and then agglomerated at 2000°F (1093°C) for 30, 60, or 90 minutes. Overall, increasing the severity of processing reduced the extent of leaching from the solids. Contrary to this expected trend are the increases in the concentration of arsenic in the leachate from agglomeration tests at 30 and 60 minutes. It is unclear as to why this occurred. Regardless of the processing steps, the spent shales did not exceed the current TCLP limits for leachability.

The concentrations of selected trace elements in raw shales from Indiana, Tennessee, and Alabama are presented in Table 6-12.²⁴ Calculations show that if all of the priority trace elements present were leached from the raw shale, the EPA limit would be exceeded only for arsenic from this sample of Alabama shale.

Embankment Design

Although the scope of work did not include a detailed design for an embankment or stockpile of raw or spent shale, the following general guidelines could be used. To ensure stability, the slope of the embankment should not exceed a rise/run ratio of 0.5 (~26.5°). A cohesion of 0 psi (0 kPa) should be assumed. The shale could be compacted to about 1.3 to 1.55 g/cm³ (80 to 95 lb/ft³) at a moisture content of 20% to 24%. Reclamation could be initiated with a surficial coverage of top soil (or overburden) of about 1 to 3 feet (0.3 to 0.9 m) in thickness. Because spent PFH shale does not exhibit the toxicity characteristic, it can be stored in ordinary surface or landfills. More severe processing (for example, agglomeration and slagging) does not appear to be warranted from an environmental standpoint.

Table 6-7. RESULTS OF TCLP TESTS CONDUCTED ON SAMPLES OF RAW INDIANA AND SPENT SHALES FROM SIX STATES

Shale Test No.	IN(NA)		AL(CH) C-14	KY(NA) C-15	OH(CL) C-16	TN(CH) C-17	MI(AN) C-28		
	Raw	C-1						C-20	
Analysis of TCLP Extract for Maximum Allowable Conc.									
Element			mg/L						
Arsenic	5	<0.01	0.076	0.021	0.01	0.15	0.039	0.012	
Barium	100	0.052	0.084	<0.02	0.10	0.057	0.088	0.034	0.014
Cadmium	1	0.084	0.083	0.039	<0.02	0.022	0.27	<0.02	0.10
Chromium	5	<0.05	0.058			<0.05			
Lead	5				<0.2				
Mercury	0.2				<0.003				
Selenium	1	0.032	--	<0.005	--	0.0085	<0.005	--	0.014
Silver	5				<0.1				

* The symbol "<" indicates the detection limit of the analytical technique used.

Table 6-8. RESULTS OF TCLP TESTS CONDUCTED ON SAMPLES
OF AGGLOMERATED (1.5 h) SPENT SHALES FROM SIX STATES

Shale Test No.		<u>IN(NA)</u> C-1	<u>AL(CH)</u> C-14	<u>KY(NA)</u> C-15	<u>OH(CL)</u> C-16	<u>TN(CH)</u> C-17	<u>MI(AN)</u> C-28
Analysis of TCLP Extract for Maximum Allowable Conc.							
Element		mg/L					
Arsenic	5	0.13	0.01	0.1	0.051	0.072	0.17
Barium	100	0.019	0.023	0.012	0.081	0.018	0.024
Cadmium	1				<0.01		
Chromium	5	0.046			<0.02		
Lead	5				<0.2		
Mercury	0.2				<0.002		
Selenium	1				<0.005		
Silver	5				<0.02		

* The symbol "<" indicates the detection limit of the analytical technique used.

Table 6-9. RESULTS OF TCLP TESTS CONDUCTED ON SAMPLES
OF AGGLOMERATED (1.0 h) SPENT SHALES FROM SIX STATES

Shale Test No.		<u>IN(NA)</u> C-1	<u>AL(CH)</u> C-14	<u>KY(NA)</u> C-15	<u>OH(CL)</u> C-16	<u>TN(CH)</u> C-17	<u>MI(AN)</u> C-28
Analysis of TCLP Extract Maximum for Allowable Conc.							
Element		mg/L					
Arsenic	5	0.54	0.051	0.54	0.11	0.31	0.39
Barium	100	0.046	0.022	0.047	0.23	0.022	0.036
Cadmium	1		<0.01		0.013	<0.01	<0.01
Chromium	5	<0.02	0.02	0.024	0.031	0.051	0.029
Lead	5				<0.2		
Mercury	0.2	<0.0015	0.0017		<0.0015		
Selenium	1			<0.010			
Silver	5				<0.05		

* The symbol "<" indicates the detection limit of the analytical technique used.

Table 6-10. RESULTS OF TCLP TESTS CONDUCTED ON SAMPLES
OF AGGLOMERATED (0.5 h) SPENT SHALES FROM SIX STATES

Shale Test No.		<u>IN(NA)</u> C-1	<u>AL(CH)</u> C-14	<u>KY(NA)</u> C-15	<u>OH(CL)</u> C-16	<u>TN(CH)</u> C-17	<u>MI(AN)</u> C-28
Analysis of TCLP Extract Maximum for Allowable Conc.							
Element		----- mg/L -----					
Arsenic	5	0.18	0.033	0.51	0.1	0.25	0.34
Barium	100	0.031	0.012	0.07	0.26	0.033	0.036
Cadmium	1	<0.01	0.014	<0.01	0.014	<0.01	<0.01
Chromium	5	<0.02	<0.02	0.032	<0.02	0.042	0.026
Lead	5	----- <0.2 -----					
Mercury	0.2	----- <0.0015 -----					
Selenium	1	----- <0.010 -----					
Silver	5	----- <0.05 -----					

Table 6-11. RESULTS OF TCLP TESTS CONDUCTED ON SAMPLES OF
SLAGGED SPENT SHALES FROM TENNESSEE AND MICHIGAN

Shale Atmosphere		<u>Tennessee</u>		<u>Michigan</u>
		Nitrogen	Air	Air
Analysis of TCLP Extract Maximum for Allowable Conc.				
Element		----- mg/L -----		
Arsenic	5	<0.010	0.032	0.049
Barium	100	0.050	0.018	0.070
Cadmium	1	<0.010	<0.010	<0.010
Chromium	5	0.19	0.070	0.087
Lead	5	<0.20	<0.20	<0.20
Mercury	0.2	0.0042	0.0018	<0.0015
Selenium	1	<0.010	<0.010	<0.010
Silver	5	<0.020	<0.020	<0.020

* The symbol "<" indicates the detection limit of the analytical technique used.

Figure 6-3. EFFECT OF PFH PROCESSING ON THE LEACHING CHARACTERISTICS (TCLP) OF INDIANA (New Albany) SHALE

Figure 6-4. EFFECT OF PFH PROCESSING AND AGGLOMERATION ON THE LEACHING CHARACTERISTICS (TCLP) OF INDIANA (New Albany) SHALE

Figure 6-5. EFFECT OF PFH PROCESSING AND AGGLOMERATION ON THE LEACHING CHARACTERISTICS (TCLP) OF KENTUCKY (New Albany) SHALE

Figure 6-6. EFFECT OF PFH PROCESSING AND AGGLOMERATION ON THE LEACHING CHARACTERISTICS (TCLP) OF OHIO (Cleveland) SHALE

Figure 6-7. EFFECT OF PFH PROCESSING AND AGGLOMERATION ON THE LEACHING CHARACTERISTICS (TCLP) OF ALABAMA (Chattanooga) SHALE

Figure 6-8. EFFECT OF PFH PROCESSING AND AGGLOMERATION ON THE LEACHING CHARACTERISTICS (TCLP) OF TENNESSEE (Chattanooga) SHALE

Figure 6-9. EFFECT OF PFH PROCESSING AND AGGLOMERATION ON THE LEACHING CHARACTERISTICS (TCLP) OF MICHIGAN (Antrim) SHALE

Table 6-12. SELECTED TRACE ELEMENTS IN RAW EASTERN OIL SHALES

State Member	Indiana New Albany		Tennessee Chattanooga	Alabama Chattanooga	TCLP Limit*
	#1	#2			
Element	----- ppm -----				
Arsenic	57.1	58.8	94.6	158.0	>100
Barium	310	240	270	350	>2000
Cadmium	<4	<4	<4	<4	>20
Chromium	33.6	31.8	42.7	35.3	>100
Lead	25	26	34	43	>100
Mercury	0.2	0.08	0.2	<0.05	>4
Molybdenum	160	170	170	260	--
Nickel	120	100	160	300	--
Selenium	<4	<4	7.5	<4	>20
Silver	<20	<20	<20	<20	>100

* Minimum concentration in solid phase to exceed TCLP limit if 100% of the element could be leached.

Conclusions

The physical properties of spent PFH shales from six states in the Eastern U.S. differ considerably. Based on the results of the tests conducted during this program, the following conclusions can be drawn:

- Thermal conductivity ranged from 0.21 for Alabama to 1.13 W/m-K for Tennessee spent PFH shale.
- Permeabilities of spent PFH shales are in the range of 10^{-2} and 10^{-4} cm/sec.
- Consolidation test results show that the void ratio (volume of voids/volume of solids) of spent PFH shales can be reduced from 1.27 to 0.38 for Michigan shale, and from 2.23 to 0.69 for Tennessee shale, respectively. The density of consolidated shale can be 65 (Michigan) to 90% (Tennessee) higher than that of the "as received" shale.
- The angle of internal friction of spent PFH shales ranges from 24.4° (Ohio) to 40.9° (Alabama). Cohesive strength ranges from 0 psi for Indiana and Alabama to 4 psi for Ohio spent PFH shales.
- Spent shale from the PFH process can be compacted to densities ranging from 1.3 to 1.55 g/cm³ (81.1 to 96.7 lb/ft³) at moisture contents of about 20 to 24%. Spent PFH shales are more friable than the raw shale tested.
- Embankments can be constructed safely a slope of 26.5° (1:2 rise/run).
- The results of leaching tests conducted with spent PFH shales indicate that none exhibit the toxicity characteristic according to the TCLP.

- Agglomeration of spent PFH shales at a temperature of 2000°F (1093°C) decreased the concentration of material leached during TCLP. Increasing the severity of agglomeration in general, decreased the concentration of material leached during TCLP.
- Slagging of selected samples of spent PFH shales at their fusion temperature further decreased the concentration of material leached during TCLP, however the difference in leachability of agglomerated and slagged samples did not appear to be significant.
- Spent shale from the PFH process can be disposed in ordinary surface or landfills.

Recommendations

Physical properties tests, as conducted on samples of spent shales from PFH processing, should be conducted on samples of agglomerated and slagged spent shales to determine the characteristics of this type of material for embankment construction. In addition, tests to determine the liquid limit (ASTM D 423) of spent PFH shales should be conducted.

Tests should be conducted to determine the effects of beneficiation on the physical and chemical properties of raw and spent PFH shales.

The effects of in-bed sulfur sorbent material (such as limestone) on the permeability and shear strength (hydration/cementation characteristics) of spent Eastern shales should be investigated.

Long-term leaching tests in large-scale lysimeters should be conducted with spent PFH shale. Trace elements, other than those specified by the TCLP, such as Ni and Mo, should be analyzed in the leachate from TCLP tests to determine the extent of leaching.

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Subtask 6.2.1. Water Availability

Introduction

Although the water-limiting aspects of oil shale processing in the Western U.S. has long been recognized, little has been done to assess the availability of water in locations where Eastern shale would be processed. The availability of water and its proximity to potential processing sites should be assessed prior to the location of any processing facility. Surface water yield data for major watersheds are available from the U.S. Geological Survey and the Corps of Engineers. Compilation and correlation of these data should yield a graphical representation of areas where the shale resource and surface water are adequate to support commercial PFH facilities.

A critical consideration in the siting of a plant to process raw oil shale is the quantity of water required for the processing system. The required quantity of water depends on several factors including the characteristics of the shale, method of processing, whether or not the water is recirculated, and the oil production capacity of the plant. The availability of water to meet the processing requirements is dependent on the type of the water source and the needs of public and other private users. The types of the water source include free flowing streams, groundwater, reservoirs, storage impoundments, or a combination of these sources.

The Eastern oil shale resource considered in this study is that located in Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee. Figure 6-10 shows the states and their proximity to each other. The locations of the shale in each of these states were taken from the literature and included those believed to be strippable based on the identification of outcrops. An initial effort was made to establish criteria for categorizing the outcrops as to their strippability; but it became apparent that a set of generic criteria could not be established. Factors such as the location of the shale stratum in the outcrop in relation to the overburden and the strippable characteristics of the overburden were not reported in the literature. Also, the economics of strippability in relation to the available energy per volume of shale versus the overburden removal costs were not investigated because of the aforementioned unknown factors. Consequently, it was assumed that where shale outcrops existed, the resource was more than adequate for supplying feedstocks to retorting facilities and that the outcropping shale could be economically strip-mined.

Objectives

The objectives of this study were to 1) determine the locations in the six states of the study region where shale was known to outcrop, 2) determine if sufficient free-flowing water sources were available for satisfying the import requirements of shale processing plants, and 3) select locations in each of the states where shale processing plants could be sited in proximity to strip-minable, outcropping shale resources and the available water source.

Figure 6-10. PROJECT STUDY AREA

Discussion

This study was based on a review of the published information about oil shale in the six states and contacts with persons within each state who were knowledgeable about oil shale. The locations within a state were selected where the oil shale appeared to crop out in stratum thicknesses of at least ten feet. Further, an assumption was made that wherever the shale unit was at least ten feet thick, it would be economical to remove and process. In each state where Fischer Assay values and shale unit thicknesses were reported, these factors were considered in choosing specific locations as a possible site for a processing plant.

In determining water availability, the approach was to use reports published by the U.S. Geological Survey (USGS) for low-flow characteristics for free flowing streams. Neither groundwater nor the potential for especially constructed impoundments by the oil shale industry were considered as sources for processing water; however, impoundments by federal agencies were considered as a water source. In general, regulated as well as nonregulated streams were viewed as potential sources. Also, only import water needs of the processing plant were used.

The net import water requirements for the water availability study were based on estimates made previously for production of oil from shale by the moving-bed hydroretorting process. The import water requirements for the pressurized fluidized-bed hydroretorting process (PFH) were assumed to be similar in magnitude for the six shales in this study. The plant import water requirements are related to the characteristics of the particular shale being processed and vary from an estimated 226 gallons per barrel (5.38 L/L) of oil produced per day for the Michigan (Antrim) shale to a maximum of 345 gallons per barrel (8.21 L/L) per day for the Kentucky (Sunbury) shale. Total daily import requirements relate directly to the plant capacity. Water import quantities are described in cubic feet per second (cfs) of stream flow, and in million gallons per day (mgd).

The selection of a specific site in relationship to the availability of processing water is governed by the laws and regulations of the state in which the site is to be located. Further, the overall capacity of free flowing streams in each state to support a processing plant was determined on the basis of current and future water users as reported in The Nation's Water Resources 1975-2000 as published by the U.S. Water Resources Council. The stream capacity is a critical determination during the plant siting process. Among the possible users are municipal water supplies, disposal of liquid wastes from industry, steam electric generation, aquatic life, etc. In many states, the legal basis for water withdrawal is tied to water quality standards that incorporate a day-year low-flow characteristic of the source stream.

The procedure used in this study was to locate the counties in each of the six states where outcrops of the oil shale were reported and possible water sources were nearby. In some instances, information on the exact location of the outcrops was not reported in the literature, therefore the general location was plotted on USGS planimetric or hydrologic unit maps. Since the oil shale outcrops were located in several counties in each of the states evaluated, a selected few of the counties were initially investigated

on the basis of the available water. Later investigations considered shale outcrops and subcrops present in all counties in each state, and the general availability of major streams in proximity to areas where the shale was reported. For each of the six states, the available USGS reports on the low-flow characteristics of streams were viewed to determine if any streams with the required quantity of flow were in the vicinity of the outcrops. Any stream with the minimum low-flow characteristics within a 25-mile (40.2 km) radius of the outcrop would most likely be a suitable source of import water for an oil shale processing plant. The regulations for the removal of water from a stream varies among the states included in the study. For example, in Tennessee the low-flow value is based on the lowest average flow in cubic feet per second for three consecutive days in a recurrence interval of 20 years. It is designated as the 3 day-20 year flow value. In Ohio, for example, it is the 7 day-10 year flow value that is used as a factor in determining withdrawal permits.

This study was essentially restricted to an analysis of the published literature; however, contacts were made with selected persons in each state who were knowledgeable about oil shale. These persons provided information that was not readily available in the open literature. The sources reviewed are reported in the References section.

The selection of sites for locating facilities utilizing the PFH process are discussed in the following paragraphs. An example is given for each of the six states for a plant with a capacity to produce either 10,000, 25,000, or 50,000 bbl per day (37.85, 94.63, and 189.3 kL/day) of raw shale oil. None of the sites selected require the storage of import water to supplement the selected water sources. If supplemental storage is included, there would be other water sources that could meet the low-flow criteria. In general, the water sources selected can support three to four times the maximum requirement of processing water.

Alabama -- Chattanooga Shale

Almost every county in the northern one-third of the state of Alabama is potentially a commercial source of shale, with the shale known to outcrop in 12 counties.¹ The extent of the shale in Alabama is shown in Figure 6-11. This study details four outcrop sites in three counties. It is estimated that the total area suitable for surface mining of the shale in Alabama covers an area of approximately 300 square miles (777 km²).²

The quantity of flow in the Tennessee River is sufficient to support large oil shale processing plants. The river is contiguous to five counties in northeast Alabama where multiple outcrop sites exist.

Outcrop sites were noted in Etowah, Jackson, and Madison Counties in northern Alabama. The site in Etowah County may be located about 5 to 6 miles (8 to 9.7 km) east of Mountainboro, Alabama on a tributary of Big Wills Creek¹ (See Figure 6-12). In Jackson County, the two sites are close to each other but are on opposite sides of the Tennessee River. The first one is located at the junction of State Routes 279 and 79 on the northwest bank of the Tennessee River. The second outcrop site is on the southeast side of the Tennessee River about 1 1/2 miles (2.4 km) northeast of Langston, Alabama¹ (See Figure 6-12). The site selected for the study in Madison County is located at

Figure 6-11. AREAL EXTENT OF THE CHATTANOOGA SHALE
IN ALABAMA AND TENNESSEE

Adapted from U.S.G.S. Alabama Hydrologic Unit Map, 1974

Figure 6-12. SITE LOCATION IN ETOWAH AND JACKSON COUNTIES

Quick Mills on Flint River about 12 miles (19.3 km) north-northeast of Huntsville, Alabama¹ as shown in Figure 6-13.

The quantities of import water and the minimum flow rate of a free flowing stream required for the Chattanooga shale from northern Alabama for three processing plant capacities as shown in Table 6-13.

The northern Alabama sites are in the Tennessee Region as defined by the U.S. Water Resources Council. The Tennessee River is the major surface water resource in the region. It has a slack-water channel for its entire length and, consequently, provides a significant source for water withdrawals. Total water withdrawals are expected to decrease by 19% from 1975 to the year 2000. However, water consumption will increase by 251% by the year 2000. The major increase in consumption will be by thermal electric plants.

Manufacturing is not expected to significantly increase water consumption between the years 1975 and 2000.³ All four Alabama sites used in this report are within 25 miles (40.2 km) of the Tennessee River. The river is the major water resource in the region, and can support more than one 50,000 bbl/day (189.3 kL/day) plant. The site in Etowah County is bounded by the Big Wills Creek and could supply water for a 10,000 bbl/day processing plant and possibly a 25,000 bbl/day facility. This creek has a 7 day-10 year low flow of 33 cfs (0.934 m³/s).⁴ The site selected in Madison County for a 25,000 bbl/day plant to process the Chattanooga shale is located on the Flint River which empties into the Tennessee River. The 7 day-10 year low-flow at the site is 67 cfs (1.90 m³/s), which is more than adequate to maintain four times the required flow during withdrawals.⁴

Indiana -- New Albany Shale

The New Albany shale and equivalent strata crop out or underlie a cover of unconsolidated deposits from Newton County in northwest Indiana to Floyd County in the southeast along the Ohio River. The shale is present in 61 counties with outcrops in 32 counties.⁵ The outcrop belt of the shale is shown in Figure 6-14. The total area of New Albany shale suitable for surface mining has been estimated to be 600 square miles (1554 km²).² The Clegg Creek member is the uppermost member of the New Albany shale and contains the highest concentrations of organic material.⁶ This report presents three outcrop sites, two of which are Clegg Creek member, in three separate counties.

The specific sites selected for this report are in Clark, Floyd, and Scott Counties. The Clegg Creek member crops out in Clark County in a road cut on Indiana Highway 160 about two miles southeast of Henryville.⁷ This site, shown in Figure 6-15, was selected as a possible choice for a 50,000 bbl/day oil shale processing plant. It was selected because it is near the Ohio River where sufficient water is available. The Floyd County Clegg Creek shale site, chosen because of its proximity to both the East Fork White River and the Ohio River, is identified as:

- "Stream cut and road cut along Quick Creek in the NE 1/4 NE 1/4 sec. 15, T4N, R. 7E., Scott County. Deputy Quadrangle."⁵

Adapted from U.S.G.S Planimetric Map of the State of Alabama, 1933.

Figure 6-13. SITE LOCATION IN MADISON COUNTY

Table 6-13. MINIMUM FLOW RATE OF WATER SOURCE FOR
THREE PLANT SIZES (Alabama)

<u>Plant Size, bbl/day</u>	<u>Required Import Water, mgd</u>	<u>Minimum Required Flow Rate of Stream, cfs</u>
10,000	2.72	4.21
25,000	6.80	10.53
50,000	13.60	21.05

The Scott County site was selected because of its proximity to the Ohio River. The Blocher member of the New Albany shale, which also has a high estimated yield,⁷ is present at this site. This outcrop location is identified as:

- "Stream cut beginning at Blackiston Mill on Silver Creek and continuing westward a quarter of a mile along Slate Run, on the north edge of New Albany in lot 63, Clarks' Grant, Floyd County. New Albany Quadrangle."⁵

Both the Floyd County and the Scott County sites are plotted in Figure 6-16.

The quantity of import water to serve three different sizes of processing plants is shown in Table 6-14. The minimum flow rate of a free flowing stream required to provide the quantities of import water is also shown in the table.

For water resources planning, the area designated as the Ohio Region encompasses much of Indiana. The primary river in the region is the Ohio, which begins at the confluence the Allegheny and the Monongahela Rivers. The area has about 170 major man-made reservoirs and many more small impoundments. In a survey review of the minor free-flowing streams where shale outcrops had been identified, it was noted that the 7 day-10 year low-flow values were inadequate to sustain a 10,000 bbl/day processing plant. The major streams, such as the Wabash and the Ohio, have 7 day-10 year low-flows sufficient to supply import water for 50,000 bbl/day plants. The Ohio River was selected as the water source for 50,000 bbl/day plants at the locations identified in Clark, Floyd, and Scott Counties. The 7 day-10 year low-flow value in the reach between Cincinnati and Louisville averages about 10,800 cfs ($305.8 \text{ m}^3/\text{s}$). In order to sustain one plant, only 17.8 cfs ($0.505 \text{ m}^3/\text{s}$) are needed for import water. The East Fork White River is also available as a water source for the site in Scott County since its 7 day-10 year low-flow rate, as measured at a gauging station within 25 miles (40.2 km) of the outcrop site, is 168 cfs ($4.76 \text{ m}^3/\text{s}$),⁸ making it also capable of supporting a 50,000 bbl/day plant.

Kentucky -- Sunbury Shale

Black shales of Devonian and Mississippian age crop out extensively along the outer rim of the Cincinnati Arch in a crescent-shaped pattern and to a lesser extent in south central Kentucky in the Cumberland Saddle region.⁹ The locations of major oil shale outcrops are shown in Figure 6-17. This area covers about 1000 square miles (2590 km^2).¹⁰ Within the State of Kentucky, black shale is found in 95 counties. The black shale crops out in 28 of these

Figure 6-14. OUTCROP BELT OF NEW ALBANY SHALE IN INDIANA

Adapted from U.S.G.S. Indiana Hydrologic Unit Map, 1974.

Figure 6-15. SITE LOCATION IN CLARK COUNTY

Adapted from U.S.G.S. Indiana Hydrologic Unit Map, 1974.

Figure 6-16. SITE LOCATION IN FLOYD AND SCOTT COUNTIES

Table 6-14. MINIMUM FLOW RATE OF WATER SOURCE FOR THREE PLANT SIZES (Indiana)

Plant Size bbl/day	Required Import Water, mgd	Minimum Required Flow Rate of Stream, cfs
10,000	2.30	3.56
25,000	5.75	8.90
50,000	11.50	17.80

Figure 6-17. LOCATION OF OIL SHALE OUTCROP AREAS IN KENTUCKY

counties.¹⁻⁷ The Mississippian aged Sunbury shale outcrops out along the eastern rim of the Bluegrass area in northeastern Kentucky (see Figure 6-18 for physiographic terminology). This report documents four Sunbury oil shale sites in three counties.

The black shale outcropping in the northern portion of Kentucky's Cincinnati Arch area encompasses four of the state's drainage basins, as Figure 6-19 illustrates.¹¹ Most of the crescent-shaped oil-shale outcrop belt is within 25 miles (40.2 km) of various points along the Kentucky and Ohio Rivers, as the 25-mile projections in Figure 6-20 show.¹² The Licking River and the Ohio River flow within range of four Sunbury shale bearing counties in the Knobs and Outer Bluegrass physiographic areas.¹³ All of the above mentioned streams exhibit abundant flows to supply water to large capacity oil shale plants.

Much research has been conducted on the Sunbury oil shale, especially in Fleming and Lewis Counties. For this report, sites were selected in those two

Figure 6-18. PHYSIOGRAPHIC AND STRUCTURAL NOMENCLATURE OF KENTUCKY (From Reference 13)

Figure 6-19. DRAINAGE BASINS SURROUNDING OUTCROP AREA IN KENTUCKY

Figure 6-20. 25-MILE PROJECTIONS FROM THE OHIO AND KENTUCKY RIVERS TO POINTS IN THE BLACK SHALE OUTCROP

counties, with one site selected in Rowan County as well. Figure 6-21 shows one site in Fleming County and two in Lewis County, with the latitude and longitude of the sites marked on Figure 6-22. The site selected in Rowan County is depicted in Figure 6-22. This Sunbury oil shale exposure site is located on the north side of Interstate 64 and about 3.2 miles from the Licking River Bridge at the Barth-Rowan County line.⁷

The gallons of import water and the minimum flow rate of a free flowing stream required for the Sunbury shale are shown in Table 6-15.

Table 6-15. MINIMUM FLOW RATE OF WATER SOURCE FOR THREE PLANT SIZES (Kentucky)

Plant Size bbl/day	Required Import Water, mgd	Minimum Required Flow Rate of Stream, cfs
10,000	3.45	5.34
25,000	8.63	13.36
50,000	17.26	26.72

The surface water withdrawal policy in Kentucky is that no more than one-tenth of average daily flow of any given stream can be withdrawn. As long as average daily stream flow is ten times greater than the daily plant requirement, the stream can be considered as a water source.¹² In this report, the possible site in Fleming County could use the Licking River as its water source for a 50,000 bbl/day plant. The Licking River near Farmers, Kentucky has an average discharge value of 1,070 cfs ($30.3 \text{ m}^3/\text{s}$), leaving a wider margin of safety than state regulations require.¹² The two possible sites in Lewis County are adjacent to the Ohio River, the primary river in the region. Its average daily discharge is 95,210 cfs ($2696 \text{ m}^3/\text{s}$).¹² The daily water withdrawal of two 50,000 bbl/day oil shale processing plant would use less than 1% of the average daily flow. The major stream for a potential source of processing water for the Rowan County site is the Licking River. A few miles upstream, the river has been dammed to form the Cave Run Reservoir. The drainage area for the Cave Run Lake is 826 square miles (2139 km^2). The flow in the river as measured at Farmers is regulated at the minimum design flow of 50 cfs. The flow rate is 3-3/4 times that required to support a 25,000 bbl/day processing plant without storage. The U.S. Corps of Engineers reservoir could serve as a source of water to augment the Licking River withdrawal site. The Corps' policy is not to consider that their reservoirs have excess capacity, but there is always the opportunity to petition for reallocation of the existing storage capacity.

Michigan -- Antrim Shale

Devonian black shale is present in 69 counties in Michigan, with the Antrim shale outcropping in 19 of these counties.⁷⁻¹⁴ Figure 6-23 delineates the presence of Devonian oil shale in the lower peninsula.⁷ It is reported that suitable surface mining of the Antrim shale covers an area of about 160 square miles (414 km^2).² This report presents eleven Antrim shale outcrop sites in four counties.

Adapted from U.S.G.S. Planimetric Map of the State of Kentucky, 1958.

Figure 6-21. SITE LOCATION IN FLEMING AND LEWIS COUNTIES

Adapted from U.S.G.S. Planimetric Map of the State of Kentucky, 1958.

Figure 6-22. SITE LOCATION IN ROWAN COUNTY

The vast water resources of Lakes Michigan and Huron appear available to 12 outcrop-bearing counties in the northern rim of the Lower Peninsula. The abundant water supply of the two lakes, along with such streams as the Sturgeon River, are demonstrably capable of supporting 50,000 bbl/day oil shale processing plants at sites within range of each water source.

Michigan's annual freshwater withdrawals in 1975 were 42,813 mgd, but it is expected to decrease to 25,623 mgd by the 2000. Withdrawals for manufacturing will have decreased by 20%. Although withdrawals will be reduced, it is estimated that consumption in the manufacturing sector will nearly quadruple between 1975 and the year 2000. Because the withdrawals are projected to decrease significantly due to reuse, water resource supplies are estimated to be adequate to meet future demands by the year 2000.¹⁵

Oil-shale outcrop sites were chosen in Alpena, Antrim, Charlevoix, and Cheboygan Counties for this report.

The site location nomenclature refers to topographic quadrangle maps in which Twp is Township, sec is Section, C is Center, T is Tier, and R is Range. Figures 6-24, 6-25, and 6-26 are plotted on planimetric maps, and not on topographic maps, for clarity in showing the locations of the sites.

The Alpena County outcrop sites shown in Figure 6-24 are individually identified as:¹⁴

- "Long Rapids Twp., sec. 15, T31N, R6E."
- "Green Twp., NW NW Sec. 21, T31N, R6E. In ditch along road approximately 1/4 mile South of Lachine."
- "Green Twp., SE sec. 36, T31N, R6E. Dump by old gold mine shaft."
- "Maple Ridge Twp., C sec. 17, T31N, R7E. 1/8 mile South of center sec. 17."
- "Wilson Twp., SE NE sec. 19, T31N, R7E."
- "Wilson Twp., NE sec. 30, T31N, R7E. Paxton quarry (Huron Portland Cement Co. quarry), and roadside north of quarry."
- "Wilson Twp., SW NE sec. 31, T31N, R7E."

The seven sites listed above are represented in Figure 6-24 by three marked locations because of the proximity of the sites. Figure 6-25 shows two locations, representing one site in Antrim County and one in Cheboygan County. The outcrop in Antrim County is identified as:¹⁴

- "Banks Twp., SW NE sec. 13 and SW NE sec. 14, T32N, R8W."

The site in Cheboygan County is identified as:¹⁴

- "Mentor Twp., SW sec 1, T34N, R3W. In bed of small stream in ravine, White farm."

Figure 6-23. AREA UNDERLAIN BY DEVONIAN BLACK SHALE IN MICHIGAN

Adapted from U.S.G.S. Planimetric Map of the State of Michigan, 1957.

Figure 6-24. SITE LOCATION IN ALPENA COUNTY

Adapted from U.S.G.S. Planimetric Map of the State of Michigan, 1957.

Figure 6-25. SITE LOCATION IN ANTRIM AND CHEBOYGAN COUNTIES

The site for a plant in Charlevoix County is identified as:¹⁴

- "South Arm Twp., CW 1/2 sec. 18, T32N, R7W."

The Charlevoix County site is plotted in Figure 6-26.

The volume of import water and the minimum flow rate of a free flowing stream required for the Antrim shale are shown in Table 6-16.

Table 6-16. MINIMUM FLOW RATE OF WATER SOURCE FOR THREE PLANT SIZES (Michigan)

Plant Size bbl/day	Required Import Water, mgd	Minimum Required Flow Rate of Stream, cfs
10,000	2.26	3.50
25,000	5.65	8.75
50,000	11.30	17.49

Both Lake Huron and Lake Michigan bound the northern portion of the lower peninsula. Recent daily consumptive requirements reached about 2.6 billion gallons (9.84 GL) out of a 73 billion gallon (275 GL) average daily outflow from the U.S. side of the lakes. This is roughly 3.5% of the total flow of the Great Lakes.¹⁵

Lake Huron is adjacent to Alpena County and is a possible water source for a plant located in that county. For this report, free-flowing streams were first considered. The Thunder Bay River near Hillman and the North Branch Thunder Bay River near Bolton are identified as possible water sources for a 50,000 bbl/day shale oil processing plant at one or more of the sites described in Alpena County. Although low-flow data on these rivers was not available, peak flow data (Thunder Bay and North Branch Thunder Bay Rivers having 5-year peak flow values of 1,090 and 2,070 cfs (3.09 and 58.6 m³/s), respectively) indicate that both have sufficient water to support 50,000 bbl/day plants which would require only 17.8 cfs.¹⁶

On the eastern bank of the lower peninsula, Lake Michigan bounds Antrim County and could be a source of processing water. However, the Jordan River near East Jordan may also be able to support a 50,000 bbl/day plant considering its 5-year peak flow value of 913 cfs (25.9 m³/s).¹⁶

The Cheboygan County outcrop site is within ten miles of a flow record station on the Sturgeon River with sufficient water for an oil processing plant. The station on the Sturgeon River near Wolverine records a 7 day-10 year low-flow value of 129 cfs (3.65 m³/s),¹⁶ which is more than seven times the required water for a 50,000 bbl/day oil shale processing plant.

As a result of glaciation, the northern lower peninsula is pockmarked by numerous lakes and streams. Since there is an abundance of these lakes in the region where the oil shale occurs, it was decided to identify a lake impoundment as the source for a 50,000 bbl/day plant in Charlevoix County. The water source site is a chain of lakes south of the town of Ellsworth, Michigan. The

water intake for the plant would be located on the St. Clair Lake in Antrim County. There are several other options for the plant location.

Ohio -- Cleveland Shale

The Cleveland shale is upper Devonian in age and is the topmost member of the Ohio shale formation.¹⁷ In Ohio, potential oil shale resources occur with the presence of Devonian black shale in 62 counties statewide. Outcrop and subcrop areas exist in 27 of those counties.⁷ The Cleveland Black shale outcrops in 9 counties.¹⁷ The outcrop and subcrop areas of Ohio's Devonian Black shales are shown in Figure 6-27.⁷ Three Cleveland shale outcrop sites in two counties are shown in this report.

The Scioto River as well as Lake Erie offer large amounts of water plausible for use by a minimum of ten counties known to contain Ohio shale outcrops. These two bodies of water each show water resources surpassing the needs of a 50,000 bbl/day plant.¹⁸

Three sample sites have been selected for this report; One in Pike County and two in Ross County. The Pike County site is shown in Figure 6-28 and is identified as:⁷

- "Proceed west on Ohio 32 about 2.4 miles past its intersection with Ohio 124 to road leading north to Elm Grove. Follow only road leading north out of Elm Grove uphill to road cuts in which Ohio shale is exposed."

The two possible plant sites in Ross County are identified as:⁷

- "Road cut on north side of U.S. 50 about 1.4 mi. west of Chillicothe City limits."
- "Copperas Mts -- proceed SW from Bourneville on U.S. 50 for 1.2 mi., turn left onto Jones Levee Rd.; proceed SE for 0.9 mi.; turn right onto Spargursville Rd.; proceed 0.4 mi. west on Storms Rd. to right-angle turn; proceed another 0.2 mi. north on Storms Rd. after making turn; turn left of Storms Rd. onto un-named road; proceed SW about 1 mi. on road which changes to dirt at foot of 300 ft. cliff above Paint Creek. Almost complete section of Ohio shale is exposed on cliff face."

Both Ross County sites are plotted in Figure 6-29.

The gallons of import water and the minimum flow rate of a free flowing stream required for the Ohio shale (Cleveland Member) are shown in Table 6-17.

The site selected in Pike County is near Elm Grove and is located in the immediate vicinity of the Long Fork and Sunfish creeks, small tributaries of the Scioto River. Although low-flow data is not reported for these two creeks, there is a possibility that they could serve as water withdrawal stations during certain periods of the year. The Pike County site, however, is within 25 miles (40.2 km) of the Scioto River. The nearest gauging station is at Higby, Ohio, and records show that the 7 day-10 year low-flow is 296 cfs (8.38 m³/s).¹⁸

Figure 6-27. EXTENT OF DEVONIAN BLACK SHALE OUTCROP AND SUBCROP AREAS IN OHIO

Adapted from U.S.G.S. Planimetric Map of the State of Ohio, 1952.

Figure 6-28. SITE LOCATION IN PIKE COUNTY

Adapted from U.S.G.S. Ohio Hydrologic Unit Map. 1974.

Figure 6-29. SITE LOCATION IN ROSS COUNTY

Table 6-17. MINIMUM FLOW RATE OF WATER SOURCE FOR THREE
PLANT SIZES (Ohio)

<u>Plant Size</u> <u>bbl/day</u>	<u>Required Import</u> <u>Water, mgd</u>	<u>Minimum Required</u> <u>Flow Rate of Stream,</u> <u>cfs</u>
10,000	2.46	3.81
25,000	6.15	9.52
50,000	12.30	19.04

The Scioto at this location serves as a drainage area above the gauging station of 5,131 square miles (13,289 km²).¹⁹

The two Ross County sites are also within 25 miles (40.2 km) of the Scioto River. The 7 day-10 year low-flow value at a gauging station near the outcrops is 204 cfs (5.78 m³/s).¹⁸ Since the import water for a 50,000 bbl/day plant would require less than 7% of the low-flow for the Pike County site, and 10% for the Ross County sites, it is unlikely that a problem of water usage caused by the plant would be detrimental to the river. It depends, however, on the quantities required by other users. The U.S. Water Resources Council describe the greatest water issue for the Scioto River at Columbus, Ohio is the large population and municipal water treatment plants in the reach above and below Columbus.⁷ In Ohio, the legal basis for water pollution control is tied to water quality standards that incorporate 7 day-10 year low-flow characteristics of the receiving stream.¹⁸

Tennessee -- Chattanooga Shale

The State of Tennessee has 64 counties containing potential oil shale resources owing to the Chattanooga shale present at various depths in those counties. Chattanooga shale in Tennessee has been extensively investigated and reported in the literature.^{1,20} The areal extent of the shale is shown in Figure 6-11. This oil shale unit occurs as surface outcrops in 30 counties in the middle portion of the state.¹ This report documents four outcrop sites of the Chattanooga oil shale in three counties in Tennessee.

In central Tennessee, two major bodies of water contiguous to eleven oil shale outcrop bearing counties are found to maintain water quantities more than sufficient to supply water for the largest size oil shale processing plant. The two are the Cumberland River and Center Hill Reservoir.

Two outcrop sites in DeKalb County, one in Jackson County, and one in White County are identified here. The location of Site A in DeKalb County is marked in Figure 6-30 and is identified as:⁷

- "Road cut at E end of Sligo Bridge over Center Hill Reservoir on U.S. 70, about 5.6 mi. E of Smithville."

Site B in DeKalb County as well as the sites in Jackson and White Counties are shown in Figure 6-31. Their locations are identified, respectively, as:⁷

Adapted from U.S.G.S. Planimetric Map of the State of Tennessee, 1958.

Figure 6-30. SITE LOCATION IN DEKALB COUNTY

Figure 6-31. SITE LOCATION IN DEKALB, JACKSON, AND WHITE COUNTIES

- (Site B) "2.25 miles south of Sligo Bridge over Center Hill Reservoir and 1.5 miles northeast of Youngs Bend School; west-facing waterfall in branch of Short Creek."
- (Jackson County) "1.8 miles northwest of church at Zion Hill on road leading to Blackman Fork; cut at sharp turn in road."
- (White County) "About 10 miles northwest of Sparta, 1.7 miles east of Peeled Chestnut on Tennessee Route 26, then 2.6 miles north; at Taylor Creek Falls."

The gallons of import water and the minimum flow rate of a free flowing stream required for the Chattanooga shale are shown in Table 6-18.

Table 6-18. MINIMUM FLOW RATE OF WATER SOURCE FOR THREE PLANT SIZES (Tennessee)

<u>Plant Size</u> <u>bbl/day</u>	<u>Required Import</u> <u>Water, mgd</u>	<u>Minimum Required</u> <u>Flow Rate of Stream,</u> <u>cfs</u>
10,000	3.36	5.30
25,000	8.40	13.00
50,000	16.80	26.00

The sites selected in DeKalb County have the availability of processing water from impounded reservoirs. The DeKalb County locations are essentially on the Center Hill Reservoir. This Reservoir is formed by the U.S. Corps of Engineers Center Hill Dam on the Caney Fork River. It lies in the Cumberland River Basin. The reservoir drainage area is 2,174 square miles (5631 km²). The reservoir has ample water available to serve the needs of a 50,000 bbl/day processing plant -- and for even larger plants. The Tennessee State regulation of maintaining 3 day-20 year low-flows is not a matter of concern at this Tennessee site. A more important issue will be the maintenance of water quality in the reaches of the lake affected by the water intake and outflow for the plant. Also, the U.S. Corps of Engineer's policy does not recognize excess capacity in the reservoir; therefore, it would be necessary to negotiate the volume of withdrawal water required.

If it was preferred not to use the reservoir as a water source, then the Cumberland River could be considered, as it is within 25 miles (40.2 km) of the DeKalb County sites, and the Jackson and White County sites as well. The 3 day-20 year low-flow of the Cumberland river at a gauging station at Carthage is 1,430 cfs (40.5 m³/s). This volume of water could support 50,000 bbl/day plants at the sites mentioned. Also, the Collins River near McMinnville is within range of both DeKalb County sites and the White County site; and with its 3 day-20 year low flow value of 49.8 cfs (1.41 m³/s), a 25,000 bbl/day plant could be supported at either location. The Jackson County site might also draw its water from the Cumberland River at Celina, where the the 3 day-20 year low-flow is 350 cfs (9.9 m³/s).²¹

Summary

This report, which was based on a review of the available literature, revealed that outcrops of oil shale exist in the six states included in the study. Further, several outcrops in each state were identified to be near adequate water supplies for siting a shale processing plant. There were three sizes of plants considered: 10,000, 25,000, and 50,000 bbl/day of shale oil. The water available at each site herein reported would sustain a plant of an identifiable size. The study was not an exhaustive study of all potential sites, but does include sites where sufficient information on outcrops and water was reported in the literature.

Should there be a desire to locate a plant in either or all of the states included in this study, a comprehensive survey of each site would be necessary to determine suitability. This comprehensive survey should include availability of land, proximity to transportation, information on current and long term water uses, and similar factors normally used in siting an industrial plant. Because of the wide availability of oil shale in each state and the proximity of water for use in processing, each state has one or more potential sites for a plant.

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Subtask 6.2.2.a. Water Treatability Studies: Biological Degradation

Objective

The objectives of this subtask is to determine suitable methods for treating wastewater generated during shale processing. The treatment categories that were investigated include biological and physical-chemical processes.

Discussion

Biological treatment of selected organic contaminants in the PFH wastewater was evaluated in this subtask. Operation of a mini-bench-scale unit (BSU) using Tennessee Chattanooga shale¹ resulted in sour water with a composition as given in Table 6-19. This list does not include inorganic compounds such as heavy metals because removal of those contaminants is discussed as part of Subtask 6.3. Heavy Metals Removal.

Table 6-19. COMPOSITION OF SOUR WATER
PRODUCED BY THE 2-lb/h SHALE MBU

<u>Compound</u>	<u>Concentration, ppm</u>
Thiocyanate	7350
Sulfides	58,500
Sulfates	7150
Acetone	200
Methyl ethyl ketone	50
Pentanone	15
Phenol	40
Methyl phenol	30
Ammonia	42,700
Acetonitrile	360
Propionitrile	40
Aniline	500
Methyl anilines	180
Pyrrole	130
Methyl pyrrole	70
C ₂ -pyrrole	15
Methyl pyridines	30
C ₂ -pyridines	5
Cyanide	45

By far, the pollutants found in the sour water at the greatest concentrations are ammonia and hydrogen sulfide, but treatment methods used for these contaminants are well known. The series of tests undertaken in this task evaluated removal techniques for compounds for which treatment is uncertain. Actual sour water from PFH processing of shale was not available for treatment in the quantities needed for evaluation purposes. A synthetic wastewater was formulated, which is similar to the wastewater expected from the PFH unit. Specifically, acetone, propionitrile, pyrrole, and thiocyanate were selected for treatability studies because they are found in the wastewater from oil shale hydrotreating and are similar in structure to many of the other compounds in the wastewater.

Biological treatment of the synthetic wastewater was evaluated because it is often a successful method of attacking organic, as well as some inorganic, contaminants in a waste. The extended aeration modification of activated sludge treatment was chosen because it is a relatively low-cost, reliable treatment alternative for industrial wastes. Extended aeration provides a long retention time, which minimizes the effects of both hydraulic and organic shocks that are sometimes typical of industrial operations.

Extended aeration was evaluated as the principal, but not necessarily sole, method of treatment of the synthetic wastewater. Physical and/or chemical processes may also be necessary for "polishing" to produce an effluent of desirable quality.

Activated Sludge

Activated sludge has long been the most popular method of reducing the concentration of organic compounds present in municipal wastewaters. Because microorganisms responsible for degrading compounds in the sewage comprise a living system, activated sludge may be considered a natural way of dealing with the waste. Industrial wastewaters also often contain biodegradable contaminants. Due to environmental awareness and regulations of recent decades, industries consider activated sludge as a viable treatment process. Frequently, a commercial waste requires little or no pretreatment and/or posttreatment when processed with the biological unit. In particular, activated sludge treatment is known for its relative simplicity, reliability, and low cost. Compared with other biological, chemical, or physical alternatives, an activated sludge reactor demands minimal operation and maintenance, especially for systems that operate near steady state. The extended aeration modification of activated sludge, which was selected for the work reported in this subtask, has the advantages of low sludge production, good sludge settling characteristics, relatively high ability to overcome organic and hydraulic shocks, and can be used to treat ammonia-containing wastewaters.

Unlike municipal wastes, an industrial wastewater may contain compounds that render it nonbiodegradable. To determine the biological treatability of an industrial wastewater, preliminary experiments must be performed. These experiments may reveal that biological treatment is not possible, that it will effectively treat some contaminants, but others must be removed first, or that biological treatment is the most practical option. The initial treatability studies are conducted in batch units to determine which individual contaminants are degradable, and advance to continuous flow studies using actual wastewater samples. The batch tests are indispensable for uncovering which of the components of the waste are vulnerable to biological attack.

Despite the fact that heterogeneous cultures are responsible for degradation of organic compounds in activated sludge, the kinetics of pure culture growth are very useful in predicting their behavior.^{3,4} A culture may be assumed, therefore, to follow the batch growth pattern,⁵ as illustrated qualitatively in Figure 6-32. Phase 1 may be termed the lag phase, in which microorganisms appear to be dormant but actually are actively preparing to metabolize substrate. It is in this phase that adaptive enzymes are produced if constitutive enzymes are inadequate. This phase is not present when only constitutive enzymes are required.^{3,5-7}

Figure 6-32. TYPICAL BATCH MICROBIAL GROWTH PATTERN

Phase 2, the logarithmic phase, is the time of most rapid growth. At this point, biomass growth is represented by first order kinetics, as given by the following equation:

$$dX/dt = uX \quad (6-1)$$

where X = biomass concentration, t = time, and u = the first order kinetic constant or specific growth rate. In the logarithmic growth period, substrate is unlimited so that the specific growth rate, which is partially dependent on substrate concentration, is constant. The relationship between substrate and specific growth rate was first proposed by Monod and is represented by:

$$u = u_m S/(K_s + S) \quad (6-2)$$

where u_m = maximum specific growth rate, S = substrate concentration, and K_s = saturation or Monod constant, which is the concentration of substrate required to cause a specific growth rate equal to half the maximum growth rate. The logarithmic growth phase, then, occurs when substrate concentration greatly exceeds K_s so that the specific growth rate u is, effectively, u_m and constant.^{3,5-7}

When substrate becomes the limiting growth factor, a culture enters the declining growth phase, and the relationship between substrate concentration and specific growth rate is manifested by a change in the growth curve from concave upward to concave downward. The specific growth rate is no longer the maximum rate, and the biomass growth rate may be expressed using the Monod equation for the specific growth rate:

$$dX/dt = u_m SX/(K_s + S) \quad (6-3)$$

Although this equation is the same as Equation 6-1 for the logarithmic growth phase with a substitution made for u , Equation 6-3 illustrates that the declining growth phase is not a first order reaction like the logarithmic growth phase. This is because the quantity representing u (as given by Equation 6-2) is a variable since substrate concentration is becoming smaller and smaller in comparison with K_s .^{3,5-7}

During Phase 4, or the stationary phase, substrate is essentially depleted. Although biological activity is occurring, the observed result is no change in the amount of biomass present. The rate of growth is equal to the rate of death or lysis. When microorganisms enter the endogenous or death phase, the rate of biomass decay exceeds the rate of biomass growth. This phase is characterized by survival of the fittest, as cells exist by feeding on other cells, and is represented mathematically by:

$$(dX/dt)_{net} = u_m XS/(K_s + S) - k_d X \quad (6-4)$$

where k_d = the microbial decay coefficient.^{3,5-7}

Development of a kinetics model for a continuous flow activated sludge unit is based on principles of batch growth kinetics but may be considerably

more involved, depending on the characteristics and operation of the reactor. A number of simplifying assumptions are typically made to produce a workable, yet beneficial, model. For example, mean cell residence time or sludge age is the most commonly accepted loading parameter and may be represented by:

$$\theta_c = VX/[Q_w X + (Q - Q_w)X_e] \quad (6-5)$$

where θ_c = mean cell residence time, V = aeration tank volume, Q = wastewater flow rate, Q_w = sludge wasting rate, and X_e = concentration of biomass in the aeration tank effluent. Another useful formula may be used to compute aeration tank volume based on the desired effluent quality:

$$V = \theta_c YQ (S_o - S_e)/X(1 + k_d \theta_c) \quad (6-6)$$

where Y = cell yield coefficient, S_o = substrate concentration in the influent, and S_e = substrate concentration in the effluent.^{3,5-7} In an actual treatment system, these equations must be used in conjunction with variables from other upstream and downstream operations and processes such as sedimentation tanks.

Metabolism of Acetone

The IUPAC name for this common chemical is 2-propanone. It is a clear liquid at room temperature and boils at 56°C. The polar liquid is miscible with water and is used as a solvent itself. Its structural formula is illustrated below.⁸

Acetone

Stephens and Dalton⁹ reported the metabolism of acetone by propane-utilizing microorganisms. Their research was conducted to determine which of two possible pathways specific bacterial species use in degrading propane. A metabolic pathway for the use of acetone as a carbon source by microorganisms was not suggested. To date, a literature search has not resulted in a proposal for a pathway by which acetone is biodegraded.

Metabolism of Propionitrile

Propionitrile is a yellow, water-soluble liquid at room temperature. It is also called propanenitrile and ethyl cyanide, and its structural formula is shown below. Propionitrile boils at 97.2°C.¹⁰

Propionitrile

Nitriles are sometimes found in plants and animals, and they are used commercially for producing herbicides and polyacrylonitrile plastics.^{11,12} Very little work has been done to determine the potential environmental effects of nitriles and to investigate biological degradation.^{11,13,14} Nitriles are thought to occur in shale oils and their by products because of reactions between carboxylic acids and ammonia from minerals present in the shale.¹³

As early as 1958, Ludzack *et al.*¹² reported that certain aliphatic nitriles could be biodegraded to yield ammonia and the corresponding carboxylic acid. Their tests were performed using water samples from the Ohio River, which were separately spiked with acetonitrile, acrylonitrile, adiponitrile, benzonitrile, lactonitrile, and oxydipropionitrile. The metabolism of each of these compounds at concentrations of 10 to 40 mg/L following acclimation periods of 20 to 125 days indicated that microorganisms capable of nitrile oxidation may be common in natural waters.¹²

DiGeronimo and Antoine¹¹ isolated a microorganism capable of metabolizing nitriles in 1976. In their studies, *Nocardia rhodochrous* LL100-21 was found to degrade several nitriles, but acetonitrile, hydroacrylonitrile, and propionitrile resulted in the best growth. Experiments were conducted using the nitrile alone, the nitrile plus ammonia, and the nitrile plus acetate in order to test the nitrile, respectively, as a source of both carbon and nitrogen, a source of carbon only, and a source of nitrogen only. All nitriles tested, except benzonitrile, allowed growth at each condition. This appeared to be the first report of organic nitriles serving as both a carbon and nitrogen source.¹¹

In the study by DiGeronimo and Antoine gas chromatography revealed that the nitriles were biologically converted to the corresponding amide and subsequently to the carboxylic acid and ammonia, thereby releasing the nitrogen for use by the organisms. The carboxylic acid may then be easily attacked using the metabolic pathway for organic acids. The exception to this pattern was propionitrile. The reactor in which propionitrile was used as the carbon or carbon-nitrogen source contained propionic acid and ammonia, but propionamide was present in negligible concentrations.

Two possible reasons were suggested for the peculiarity of propionitrile degradation. Because the rate of disappearance of propionitrile was slower than that of acetonitrile, it could be that the rate limiting reaction in the metabolism is conversion of propionitrile to propionamide. This would prevent an accumulation of propionamide in the reactor since its conversion to propionic acid would be relatively instantaneous. (This is analogous to the more familiar environmental process of nitrification in which ammonia is biologically converted to nitrite and then nitrate. The rate determining step is nitrite production, so that whatever nitrite appears is immediately converted to nitrate, resulting in detection of very little nitrite in the system.) A second possibility for propionitrile degradation, however, is an enzymatic pathway that is entirely different from that of other nitriles.

Nocardia rhodochrous LL100-21 was also used to study nitrile biodegradation by Collins and Knowles¹⁴ and later by Linton and Knowles.¹⁵ The first investigation verified that *Nocardia rhodochrous* LL100-21 is able to use a wide variety of aliphatic nitriles. Additionally, it illustrated the

ability of the organism to use benzonitrile as a carbon and nitrogen source. Like propionitrile degradation, benzonitrile metabolism was not accompanied by detection of benzamide.¹⁴

The Linton and Knowles investigation centered around the activities of two enzyme types which they labeled nitrile hydratase and amidase. The first catalyzes the nitrile to amide reaction while the second catalyzes the amide to acid reaction. Propionitrile was found to be an excellent inducer of both enzyme types, but the hydrolysis of propionitrile in the presence of a nitrile hydratase was very slow. This approach to the study of propionitrile metabolism supported the hypothesis that the rate limiting step in propionitrile degradation is its conversion to propionamide and, hence, propionamide is never present in appreciable quantities due to its rapid conversion to propionic acid.¹⁵

Aislabie and Atlas¹³ conducted a different yet related study. They obtained an enrichment culture that used nitriles as a nitrogen source but not as a carbon source. An alternative carbon source (such as glucose) was provided. The application of this culture to shale oils resulted in removal of the nitrogen contained in nitriles without disturbing hydrocarbons in the oil. Heterocyclic nitrogen compounds, however, which are another major source of nitrogen in shale oils, were not attacked.

Metabolism of Pyrrole

Pyrrole, also known as azole, is a heterocyclic organic nitrogen compound, the structural formula of which is shown below. The compound exists as a dark brown liquid at room temperature, has a boiling point of 130°C and is only slightly water soluble.⁸

Pyrrole

Although microbial degradation of pyrrole is not well documented, two studies involving biodegradation of carbazole were found. Carbazole is dibenzopyrrole and would likely not be as readily biodegradable as pyrrole because of the benzene rings. The structure of carbazole is shown below.⁸

Carbazole

Fedorak and Westlake¹⁶ reported aerobic degradation of alkyl carbazoles found in Norman Wells crude oil. Inoculum for the studies was obtained from a beach that had been contaminated with aviation fuel. The heterogeneous culture was grown in a mineral medium with carbazole as the sole carbon source. The results showed that the population was capable of degrading not only carbazole but also alkyl carbazoles and a number of non-nitrogen compounds such as alkanes and isoprenoids.¹⁶

A second study was reported by Finnerty, Shockley, and Attaway¹⁷ in which carbazole served as the source of nitrogen, energy, and carbon. Excellent growth of the cultures was observed. Several other compounds including pyrrole, were tested for their ability to support growth of the population that had originally been enriched using a carbazole-containing medium. Pyrrole successfully served as a nitrogen source in the presence of the carbon source succinate, but growth did not occur when pyrrole was the sole source of both carbon and nitrogen.¹⁷

Metabolism of Thiocyanate

A number of thiocyanate salts exist, all of which are very water soluble. The salt used in this study was sodium thiocyanate, which is illustrated below. The compound is a white crystal at room temperature, and its melting point is 287°C.⁸

Sodium Thiocyanate

Thiocyanate is by far the most biochemically complex of the four compounds evaluated in this subtask. Sources do not even agree as to whether it is organic or inorganic, and both autotrophic and heterotrophic organisms have been found that utilize thiocyanate.¹⁸ A number of references were found in which thiocyanate was a component in the wastewater being treated. Thiocyanate removal efficiency had considerably greater variability than that of other contaminants, but the reason for variability was unclear. The majority of references addressing thiocyanate as a wastewater pollutant dealt with coal conversion. Processes such as coal coking and coal gasification generate wastewaters that are similar to those expected from PFH processing of shales. Because of the scarcity on research of Eastern oil shale wastewater treatment, TTU relied on coal conversion research for thiocyanate treatment methods.

Ludzack and Schaffer¹⁹ conducted activated sludge experiments with cyanide, cyanate, and thiocyanate as synthetic wastewater contaminants. Thiocyanate concentrations as high as 400 mg/L were treated, and removal efficiencies of 90 to 99% were reported. The hydraulic residence time (HRT) of the experiments was not mentioned, and pH varied from 6.7 to 7.5. The authors suggested that thiocyanate metabolism could be represented by the following reaction:

The claim was made that free oxygen is not necessary for degradation, but that sulfide and ammonia produced in the above reaction may react with oxygen to produce sulfate and nitrate. Limited analytical procedures at that time (1960), however, prevented verification of the proposed overall reaction.

A biological study by Kostenbader and Flecksteiner²⁰ included both pilot plant and full-scale activated sludge treatment. The principle contaminant and the one for which treatment was geared was phenol. The HRT was low, ranging from 1.6 to 4.4 hours, and the pH was typically above 7.3. Removal efficiency for thiocyanate averaged 70% but was not consistent, with removals as low as 10% and as high as 99% observed.²⁰

Ganczarczyk and Elion²¹ reported biological treatment of a coke plant effluent by extended aeration. At the full scale plant, intentional sludge wasting was not practiced. Although this option made maintenance and operation simple, it resulted in undesirable solids concentrations in the effluent. During the period of study, the plant size was doubled, so the HRT of 14 hours was approximately doubled to 24 hours. The average pH of the effluent was 7.3 before expansion and 7.8 following expansion. Thiocyanate removal changed little due to the increased residence time. The original treatment efficiency was 52.5% with an average of 106 mg/L thiocyanate in the effluent. The larger plant size resulted in a 58.8% thiocyanate removal, or about 80 mg/L thiocyanate exiting the reactor. As with the Kostenbader and Flecksteiner study,²⁰ the phenol removal efficiency was greater than 99%.²¹

A coal gasification wastewater was biologically treated by Luthy, Sekel, and Tallon.²² HRT's of 9.2 to 18.6 days were used to achieve nitrification. Wastewater was diluted to 20, 33, and 40% of the original strength to determine optimum operating conditions. Phenolics were again the principle wastewater contaminant, ranging from 3700 to 6500 mg/L in the influent, and thiocyanate was present at an average concentration of 140 mg/L. Dilutions of both raw wastewater and ammonia-stripped wastewater were consistently treated to levels of less than 10 mg/L thiocyanate. Reactor pH was maintained at 7.0 to 7.5.²²

Luthy²³ compared biological treatment of coal coking and coal gasification wastewaters. HRT's of 1.8 to 5.7 days for coking wastes and 2.1 to 3.0 days for gasification wastes resulted in effluent thiocyanate concentrations of less than 10 mg/L consistently. The original thiocyanate concentrations were 208 to 510 mg/L and 80 to 200 mg/L, respectively. Although coking and gasification wastes were quite different, both contained phenolics at considerably higher concentrations than those of thiocyanate species. A pH of 7.0 to 7.5 was typical for treatment of both wastewaters. Luthy reported a low cell yield for thiocyanate of 0.28 mg cells per mg thiocyanate, which necessitated a long mean cell residence time.²³

Combined mine water and tailings impoundment water were biologically treated by Mudder and Whitlock.²⁴ The combined wastes contained a thiocyanate concentration of 50 to 70 mg/L and were treated to levels of less than 1 mg/L thiocyanate by both rotating biological contactors and fill-and-draw activated sludge reactors. Activated sludge failure at 60 days was attributed to metals toxicity, and it was concluded that pretreatment for metals was necessary.²⁴

Shivaraman *et al.*²⁵ investigated the effect of phenol and cyanide on thiocyanate biodegradation. An HRT of 8 to 12 hours was used, and the initial thiocyanate concentration was 104 to 133 mg/L. At phenol concentrations greater than about 1250 mg/L, thiocyanate removal efficiency decreased. Thiocyanate sulfur was present in the reactor effluent as sulfate.²⁵

Neufeld, Mattson, and Lubon¹⁸ reported the most extensive study involving thiocyanate. In order to answer several questions regarding biodegradation of thiocyanate, their synthetic wastewater contained thiocyanate as a sole carbon source. Although results of such a study are far from what is expected in a "real world" situation, they provide numerous insights into the degradation of thiocyanate in more realistic circumstances.

The pH was strictly maintained in the range of 6.7 to 7.2 in their activated sludge reactors. In addition to a phosphate buffer, acid or base was added as necessary to control pH. Operation at pH values below 6 or above 8 resulted in seriously hindered thiocyanate treatment, and a pH as near 7.0 to 7.2 as possible was recommended. Based on these results, the metabolism of thiocyanate is considered to be pH inhibited.¹⁸

Another inhibitory factor is thiocyanate concentration itself.¹⁸ In other words, there is some concentration of thiocyanate that prevents normal microbial growth, and as thiocyanate concentration increases, it eventually reaches a toxic level. The rate of substrate utilization in a substrate inhibited system is given by:

$$u = u_m / [1 + (K_s/S) + (S/K_i)^n] \quad (6-8)$$

where u_m = maximum substrate utilization rate, S = substrate concentration, K_s = saturation constant, K_i = inhibition constant, and n = order of inhibition. Graphical representation of substrate inhibition is shown in Figure 6-33. This curve is different from conventional Monod substrate utilization in that it reaches a maximum velocity and then decreases rather than asymptotically approaching a particular substrate concentration. When K_i is large, Monod kinetics are simulated. The study by Neufeld, Mattson, and Lubon indicated that thiocyanate utilization is represented by:

$$u = 2.24 / [1 + 5/[SCN^-] + ([SCN^-]/1340)^6] \quad (6-9)$$

This equation yields a maximum velocity at a thiocyanate concentration of about 470 mg/L. Above this value, therefore, substrate concentration would be expected to hinder its own metabolism.¹⁸

In addition to substrate inhibition and pH inhibition, Neufeld, Mattson, and Lubon described complicated interrelationships that exist between thiocyanate removal, phenol removal, and ammonia removal. As indicated by Shivaraman *et al.*²⁵ as well, high phenol concentrations can interfere with thiocyanate metabolism. Thiocyanate, in turn, tends to hinder phenol degradation, and phenol is inhibitory to nitrification (but ammonia is produced by thiocyanate metabolism). These relationships are further complicated by the narrow pH range recommended for thiocyanate degradation, since phenol lowers pH and ammonia raises pH. Since all three of these contaminants are present in both coal conversion wastes and the expected PFH wastewater, each system

Figure 6-33. EFFECT OF SUBSTRATE INHIBITION ON SPECIFIC GROWTH RATE

must be analyzed separately according to waste characteristics, desired effluent concentrations of each pollutant, and results of laboratory treatability studies.¹⁸

The primary overall reaction for thiocyanate metabolism was given by Neufeld, Mattson, and Lubon as:

Although this reaction is in disagreement with Equation 6-7 presented by Ludzack and Schaffer,¹⁹ high levels of nitrogen and sulfur recovery through sulfate and ammonia or ammonium in the effluent verified this reaction, which had also been presented by other researchers. Possible secondary reactions given by Neufeld, Mattson, and Lubon were:

These reactions might occur in oxygen-deficient conditions, and it may have been such a situation that led Ludzack and Schaffer to propose the production of hydrogen sulfide gas as a primary result of thiocyanate biodegradation. The liberation of ammonia upon thiocyanate metabolism indicates that a supplementary source of nitrogen is not necessary. Neufeld, Mattson, and Lubon used thiocyanate successfully as both the sole carbon source and sole nitrogen source.

Results of the Neufeld, Mattson, and Lubon study were promising. Influent concentrations of 1000 mg/L thiocyanate were treated in several continuous flow activated sludge reactors using an HRT of 24 hours. Mean cell residence time was varied from 6.7 to 216.6 days. Each unit had an average effluent thiocyanate concentration below 11 mg/L. No settling difficulties were encountered with the thiocyanate sludge, but it was pointed out that this was a one-substrate sludge, unlike any which would be encountered in an actual treatment facility. The authors suggested a mean cell residence time of at least 6.5 days be used in thiocyanate degradation.

Experimental Methods

Prior to biological treatability experiments, heterogeneous populations of microorganisms were acclimated to acetone, propionitrile, pyrrole, and thiocyanate as sole carbon sources. Acclimation was achieved in solutions containing the four substrates both individually and in combinations of 2, 3, and 4 substrates. Concentrations of the substrates in the acclimation vessels were 150 to 600 mg/L, as this was the concentration range at which original substrates were expected to be in treatability experiments. In addition to the substrate or substrate combination, essential inorganic nutrients were also included in the synthetic wastewater solutions so that acclimation would not be hindered. These nutrients and minerals and their concentrations are listed in Table 6-20.

Table 6-20. SYNTHETIC WASTE COMPOSITION

<u>Nutrient or Mineral</u>	<u>Concentration</u>
	--- mg/L --
$(\text{NH}_4)_2\text{SO}_4$	500
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	10
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.5
CaCl_2	7.5
KH_2PO_4	526
K_2HPO_4	1070
Tap water	100

Biological seed was obtained from a municipal wastewater treatment plant. Cultivation of acclimated microorganisms began using 250 ml Erlenmeyer flasks in a shaker apparatus. As this point, only solutions containing the individual substrates in concentrations of 150, 300, and 600 mg/L were used. This made it possible to determine exactly which of the four contaminants the microorganisms would be able to use as substrates.

Three days after inoculation, shaking was temporarily halted to allow any particulates that might have formed in the shaker flasks to settle. Half the flask contents were vacuumed and used to seed new shaker flasks. The old flasks were restored to volume using nutrient and substrate stocks in the appropriate amounts. This procedure was repeated, using supernatant from the second generation flasks to seed a third set of flasks. At each point during this process, sterile petri dishes containing nutrient agar were streaked with cultures from the shaker flasks to determine if viable microorganisms were present.

Following the three serial transfers of microorganisms to new growth media, agar plates revealed healthy cultures of microorganisms in each shaker flask. At this time, flasks were again settled, and the supernatant was removed for use as seed in 1.5-liter acclimation vessels. Cultures in the shaker flasks were maintained by allowing them to settle every 2 to 3 days, removing approximately half the flask contents as supernatant, restoring the flask to volume using nutrient and substrate stock solutions. Maintenance of the shaker flasks continued until heavy microbial populations were developed in the 1.5-liter acclimation reactors.

The 1.5-liter acclimation vessels were tall, cylindrical reactors, which were aerated using compressed air flowing through diffuser stones. A heavy heterogeneous population was cultivated and kept acclimated in these reactors by supplying new substrate and nutrients twice weekly. At these times, the air supply was temporarily stopped, and one third of the mixed reactor contents was removed. The mixtures were then settled, and a second third was vacuumed as supernatant and discarded. Substrates, nutrients, and distilled water were then used to bring the reactors back to volume and to the appropriate concentrations.

Upon development of dense microbial populations in the acclimation reactors, batch treatability experiments were begun. The first batch experiments involved acetone, propionitrile, and pyrrole at original concentrations of 150, 300, and 600 mg/L, respectively. These experiments were initiated by placing 25 mL biological seed from the appropriate acclimation reactor into another 1.5-liter reactor containing a solution of nutrients, minerals, and the desired amount of substrate. Reactor contents were allowed to mix briefly using aeration, and a "time zero" sample was taken. The sample was filtered through a 0.45 μ m membrane filter. Other samples were taken and filtered at intervals of 2 to 24 hours, depending on the length of the experiment and the pattern of substrate removal with time, as predicted by rough preliminary experiments.

Upon completion of individual substrate experiments using acetone, propionitrile, and pyrrole, respectively, as sole carbon sources, multiple substrate experiments were begun. Double substrate experiments were performed using each combination of two substrates at 300 mg/L each. Following these studies, thiocyanate was added as the fourth synthetic wastewater contaminant. Single substrate thiocyanate experiments were conducted using initial concentrations of 50, 100, and 300 mg/L (these concentrations were lower than those of the other three substrates because of difficulties in degrading thiocyanate, as reported in the literature). Double substrate batch experiments were performed using thiocyanate with each of the three other contaminants. The final batch study included 150 mg/L each of the four substrates. Duplicates were conducted of each experiment to confirm reproducibility to the extent that is possible with heterogeneous biological systems.

All samples were analyzed for chemical oxygen demand (COD) using the closed reflux, ampule variation of colorimetric analysis, as specified in Standard Methods.²⁶ In experiments containing multiple substrates, analysis for each organic compound was accomplished using gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS). A Hewlett-Packard 5890A was used for gas chromatography analyses while a Hewlett Packard 5890A with headspace sampler was used for gas chromatography/mass spectrometry analyses. Thiocyanate concentrations were determined by the colorimetric procedure for cyanides amenable to chlorination, as specified in Standard Methods.

Following batch experiments, which revealed each single substrate and substrate combination to be biologically degradable, continuous flow experiments were performed. A diagram of the reactor used is shown in Figure 6-34. A Masterflex Pump Model 7567-70 was used for all continuous flow units. The first continuous flow biological reactor was actually begun before batch studies were completed. This unit was fed acetone as the sole carbon source and served the purpose of acquainting the TTU project staff with operation and maintenance of a continuous flow reactor. Sludge which settled in the clarifier unit was returned to the aeration tank twice daily.

Reactor 1 was fed a solution containing about 150 mg/L each of acetone, propionitrile, pyrrole, and thiocyanate in addition to essential nutrients and minerals. Initially, an HRT of 5 days was used. This residence time was gradually decreased depending on the performance of the biological reactor. As with the acetone reactor, settled sludge was recycled twice daily. Several months after Reactor 1 was begun, Reactor 2 went online. This unit was fed a

Figure 6-34. DIAGRAM OF THE CONTINUOUS FLOW UNIT USED IN TREATABILITY STUDIES

solution that contained, in addition to excess nutrients and minerals, about 400 mg/L thiocyanate, 300 mg/L acetone, 100 mg/L propionitrile, and 50 mg/L pyrrole. This feed mixture more closely resembled that expected from the PFH unit with the exception of thiocyanate, the treatability of which at higher levels (such as those expected in the PFH waste) was unknown. Reactor 2 was begun using a 3-day HRT, which was gradually decreased based on experimental results. With both reactors, when the minimum practical HRT was reached, the organic strength of the influent was increased to further evaluate the performance of the unit.

Results and Discussion

The results of batch experiments using acetone as a single substrate are shown in Figure 6-35. COD was used in single substrate experiments to indicate substrate concentration change. When 600 mg/L acetone (in addition to inorganic nutrients and minerals) was present initially, the solution exerted a COD of 873 mg/L. The reactor was seeded with acclimated microbial culture, and after 44 hours of aeration, the COD was reduced to 27 mg/L. Additional aeration did not result in further decrease in COD. This corresponds to a COD removal efficiency of 97%. The COD cannot be expected to reach zero (as could be expected with a specific substrate removal parameter), because inorganics and extraneous metabolic by-products also exert a COD.

An initial acetone concentration of 300 mg/L resulted in an original COD of 594 mg/L. Following 29 hours of biological treatment in batch, a minimum COD had been reached. The final COD of 20 mg/L yielded a removal efficiency of 97%.

The final concentration of acetone used in single substrate experiments was 100 mg/L. This solution exerted 199 mg/L COD. Within 31 hours of aeration with microbial seed, this solution contained a COD of 31 mg/L. Biological treatment efficiency, based on COD, was 84%.

A qualitative mention of kinetics is warranted at this point. Because acclimated cultures were used for seed in all experiments, upon initiation of an experiment, microorganisms should almost immediately enter the logarithmic, or first-order, growth phase. This causes substrate to be depleted by first order kinetics as well. The substrate removal plots shown in Figure 6-35 appear to be governed by first order reactions, and linear portions on semi-logarithmic plots confirmed first order removal of acetone.

Figure 6-36 illustrates the removal of propionitrile in batch activated sludge reactors. A COD of 884 mg/L was exerted by a solution containing about 600 mg/L propionitrile initially. A minimum COD of 24 mg/L was reached after 49 hours of biological treatment representing a removal efficiency of 97%.

An aeration time of 47 hours was necessary to minimize the COD of a synthetic waste solution containing about 300 mg/L propionitrile. The original COD of 527 mg/L was reduced to 29 mg/L within this time for a removal efficiency of 94%.

A solution containing 100 mg/L propionitrile exerted a COD of 202 mg/L. Following 31 hours of biological treatment in batch, a minimum COD of 26 mg/L was reached. COD-based removal efficiency was 87%. Figures 6-35 and 6-36

BIOLOGICAL REMOVAL OF ACETONE

Figure 6-35. BATCH EXPERIMENTS USING ACETONE AS SINGLE SUBSTRATE

REMOVAL OF PROPIONITRILE

By Biological Treatment

Figure 6-36. BATCH EXPERIMENTS USING PROPIONITRILE AS SINGLE SUBSTRATE

illustrate that removal patterns were very similar for acetone and propionitrile in batch. In each case, 49 hours or less was necessary to minimize COD. As was the case with acetone, semi-logarithmic plots of propionitrile experiments revealed that the substrate was being removed at a rate consistent with first-order kinetics.

Batch biological treatment of pyrrole is illustrated in Figure 6-37. Using an initial pyrrole concentration of about 600 mg/L, 80 hours was required to reduce to COD. COD-based treatment efficiency of 97% was evident when the COD was reduced from an initial level of 1155 mg/L to a final level of 35 mg/L.

A COD removal efficiency of 90% was possible using batch activated sludge for a synthetic waste solution containing 300 mg/L pyrrole. The original COD in this reactor was 580 mg/L. The minimum COD of 59 mg/L was achieved in 61 hours.

For batch treatment of a 100 mg/L pyrrole solution, 54 hours of aeration was necessary. During this time, 92% of the original COD was removed, resulting in a residual COD of 20 mg/L. Although the removal of pyrrole could be modeled by first order kinetics, its removal was not similar to those of acetone and propionitrile. Degradation of pyrrole required considerably more time, as much as 80 hours. The absence of a lag in substrate removal, however, indicated that microorganisms were well acclimated to pyrrole as a sole source of carbon.

The metabolism of thiocyanate in batch was different from that of the three other single substrates. Lag phases of 87 to 168 hours were observed in these experiments. Although several weeks of acclimation to thiocyanate as a sole carbon source had been allowed before beginning the batch studies, these results indicated that microorganisms were not well acclimated. Additional time for cultivation was used before repeating the experiments. Seed from reactors utilizing other substrates was also added to make sure there was adequate microbial population for degrading thiocyanate. Because thiocyanate had been reported in the literature as difficult to degrade, initial thiocyanate concentrations of 300, 100, and 50 mg/L were employed in these studies instead of 600, 300, and 100 mg/L, the initial concentrations used in the other experiments. As shown in Figure 6-38, none of these measures was successful in eliminating the lag phase in batch.

The highest initial thiocyanate concentration used in batch experiments was 300 mg/L. A lag phase of 87 hours was observed. Within 120 hours of additional treatment, the COD, which was originally 400 mg/L was reduced to 44 mg/L representing a removal efficiency of 89%.

When microbial seed was added to a synthetic waste solution containing 100 mg/L thiocyanate, a lag phase of 168 hours occurred before degradation began. At that point, the COD was about 170 mg/L. Following 70 hours of additional aeration, 79% of the original COD had been removed by biological metabolism. A residual COD of 36 mg/L resulted.

The final thiocyanate concentration attempted in batch experiments was 50 mg/L. This initial thiocyanate level exerted a COD of 110 mg/L and caused a lag phase of about 168 hours. About 120 hours of biological treatment was

BIOLOGICAL REMOVAL OF PYRROLE

Figure 6-37. BATCH EXPERIMENTS USING PYRROLE AS SOLE CARBON SOURCE

BIOLOGICAL REMOVAL OF THIOCYANATE

Figure 6-38. BATCH EXPERIMENTS USING THIOCYANATE AS CARBON SOURCE

required following the lag phase to reduce the COD to 39 mg/L. COD removal efficiency was 65%.

Thiocyanate, thus, was biologically treatable, as evidenced by the eventual reduction in COD. A considerable lag phase, however, was not eliminated in batch studies. Semi-logarithmic plots of thiocyanate experiments confirmed that thiocyanate removal from the system was governed by first-order kinetics.

Double substrate experiments involving acetone, propionitrile, and pyrrole were analyzed using gas chromatography. Results of these experiments revealed that substrates were being metabolized simultaneously rather than sequentially. Practical implications of this finding are reduced HRT, reactor volumes, and power requirements in an actual treatment facility. An example of a double substrate experiment is illustrated in Figure 6-39. The synthetic waste solution treated in batch in this experiment included 300 mg/L each propionitrile and pyrrole initially. The propionitrile concentration was reduced to less than 1 mg/L in 59 hours, and pyrrole reached a level of 7 mg/L in 118 hours of biological treatment. The metabolism of propionitrile in this experiment was similar to the metabolism of propionitrile as a single substrate. Pyrrole was not degraded as rapidly in this experiment as it was in the single substrate experiments. COD removal efficiency in this test was 94%, with 54 mg/L COD remaining after 118 hours of aeration.

In experiments involving acetone-propionitrile and acetone-pyrrole pairs, metabolism of each substrate was very similar to that observed in single substrate experiments. GC/MS analyses were performed on the acetone-propionitrile study to determine if other biological by-products might be present at any point during the experiment. No by-products other than carbon dioxide were detected. This experiment also revealed that acetone and propionitrile were metabolized at almost identical rates.

Double substrate experiments including thiocyanate were different from those including pairs of only acetone, propionitrile, and pyrrole. An example is shown in Figure 6-40, which illustrates the metabolism of a synthetic waste solution containing 300 mg/L each of propionitrile and thiocyanate. Two distinct phases of COD reduction are evident on the graph, both of which may be modeled by first-order kinetics, as revealed by semi-logarithmic plots. The first sharp decrease in COD may be explained by metabolism of propionitrile. During this 46-hour period, the COD was reduced from 1012 mg/L to 398 mg/L. The time is similar to that required to metabolize propionitrile as a single substrate. The second sharp drop in COD occurred between 100 and 150 hours. Following a lag phase from 46 to 70 hours, the COD began to decrease and then dropped more rapidly beginning with 150 hours. This second first-order curve may be attributed to the degradation of thiocyanate. After 150 hours of additional treatment, COD removal efficiency was 94%, with a residual COD of 60 mg/L.

At first glance, it might be concluded that the experiment including propionitrile and thiocyanate is a simple case of sequential metabolism, with propionitrile being degraded preferentially over thiocyanate. This assumption cannot be correctly made, however, because of the lag phase present when thiocyanate was degraded as a single substrate. When 300 mg/L thiocyanate was available as a sole carbon source, a lag phase of 88 hours was observed. This

REMOVAL OF TWO SUBSTRATES

300 mg/L Propionitrile and Pyrrole Initially

Figure 6-39. DOUBLE SUBSTRATE EXPERIMENT USING
PROPIONITRILE AND PYRROLE

REMOVAL OF TWO SUBSTRATES

300 mg/L Propionitrile and SCN⁻ Initially

Figure 6-40. DOUBLE SUBSTRATE EXPERIMENT USING
PROPIONITRILE AND THIOCYANATE

is similar to the time at which the metabolism of thiocyanate began in the propionitrile-thiocyanate experiment. Based on this study alone, therefore, no conclusion may be reached regarding the preference of propionitrile as a carbon source. Batch experiments using synthetic wastes containing thiocyanate and either acetone or pyrrole were also characterized by two distinct log phases of substrate removal.

The final multiple substrate batch experiment included 150 mg/L each of the four substrates. As illustrated in Figure 6-41, the most rapidly metabolized carbon source was propionitrile, which was present at less than 1 mg/L within 30 hours of batch activated sludge treatment. Acetone was degraded almost as rapidly and was less than 1 mg/L at 45 hours. The removal of pyrrole was much more gradual, requiring 93 hours to reach the 1 mg/L analytical detection limit. Although a lag phase of about 45 hours occurred in the metabolism of thiocyanate, this lag is significantly lower than that present in single- and double-substrate studies. An additional 48 hours of aeration decreased the thiocyanate concentration to less than 1 mg/L. COD removal efficiency was 98%, leaving a residual COD of 17 mg/L after 93 hours, while removal of each individual substrate exceeded 99%.

The batch activated sludge experiments demonstrated that all four substrates were biologically degradable. The next step was to conduct continuous flow studies with the four compounds. The first continuous flow unit was operated to acquaint lab personnel with procedures involved in maintaining the reactor. This unit received a feed stream containing 600 mg/L acetone as the sole carbon source. The reactor went online at an HRT of 96 hours and produced an effluent containing an average COD of 32 mg/L. A reduction in HRT to 48 hours resulted in 40 mg/L COD in the effluent. The flow was finally increased to correspond to a 24-hour HRT. This change yielded a steady-state effluent with a COD of about 70 mg/L. Operation of this unit was discontinued so that studies using a synthetic waste containing all four contaminants could begin.

Two continuous flow reactors were used for the treatability studies. Reactor 1 went online first and was fed equal concentrations of acetone, propionitrile, pyrrole, and thiocyanate. Reactor 2 was initiated and was fed a synthetic waste with a composition similar to that expected from the PFH process. Both reactors were begun at relatively high HRT's, and the flows were gradually increased. Feed strengths were then increased to further test the performance of the reactors.

The original feed stream to Reactor 1 contained 150 mg/L each of the four substrates. Reactor performance is shown in Figure 6-42. Only COD values are shown in Figure 6-42 for simplification. Reactor 1 was initiated at a HRT of 5 days. The average COD of the feed stream was 974 mg/L, and a steady-state COD of 90 mg/L was achieved in the effluent. On most days, original substrates were less than 1 mg/L in the effluent, and the greatest concentration of any substrate in the effluent was 4 mg/L.

Following 47 days of operation at an HRT of 5 days, the flow to Reactor 1 was increased to yield an HRT of 3 days. The reactor was allowed to operate under these conditions for a total of 21 days. The feed strength was unchanged, and average effluent COD was 34 mg/L. No original substrates were above the 1 mg/L detection limit in the effluent. Based on these results, the

REMOVAL OF FOUR SUBSTRATES

By Biological Treatment

Figure 6-41. MULTIPLE SUBSTRATE EXPERIMENT USING ACETONE, PROPIONITRILE, PYRROLE, AND THIOCYANATE

CONTINUOUS FLOW REACTOR 1

Figure 6-42. PERFORMANCE OF REACTOR 1

HRT of Reactor 1 was further reduced to 2.5 days. Steady-state performance at this flow rate was characterized by an effluent with an average COD of 42 mg/L, and no original substrates were detected. The reactor was operated a total of 47 days before increasing the flow to give an HRT of 2 days. This resulted in an effluent containing about 43 mg/L COD and original substrates below the 1 mg/L detection limit. These operating conditions were maintained for 27 days.

The flow was further increased so that the HRT would be 1.5 days. This flow rate was used for 24 days and produced an average of 71 mg/L COD in the treated wastewater. No original substrates were above the 1 mg/L detection limit in the effluent. An HRT of 1.25 days was then maintained for 19 days, during which time original substrates remained below 1 mg/L, and COD averaged about 53 mg/L in the effluent. Based on these results, the HRT was adjusted to 1 day. At this flow rate, an average COD of 69 mg/L was observed in the effluent, but original substrates were below the 1 mg/L detection limit.

Reactor performance was evaluated following the 1-day residence time experiment. The effluent water quality had remained high throughout the operation of Reactor 1. The effluent was also easily filterable, and sludge had good color and settling characteristics. Therefore, to further test the treatment capacity of the reactor, the feed strength was increased. A new influent containing about 200 mg/L of each substrate was prepared, and the HRT was unchanged.

The feed containing 200 mg/L of each substrate was used for Reactor 1 for 14 days. During this time, an average COD of 62 mg/L was observed in the effluent and original substrates were below 1 mg/L. Influent concentrations were increased to 300 mg/L each, producing an effluent COD of about 99 mg/L. Original substrates remained below the 1 mg/L detection limit. Following 12 days of operation with the feed containing 300 mg/L of each substrate, the influent concentrations were changed to 400 mg/L each. This feed was used for a total of 49 days. Original substrates were typically below 1 mg/L in the effluent, but occasional substrate breakthroughs were observed, the greatest of which was 11 mg/L. The average COD in the effluent was 117 mg/L.

When the feed to Reactor 1 was increased to a strength of 500 mg/L of each substrate, reactor performance changed considerably. Sludge in the unit, which had been light brown previously, became lighter in color. The quantity of sludge increased, and settleability worsened. The increase in the substrate to microorganism ratio caused the reactor population to shift to the logarithmic growth phase. In a typical activated sludge unit, decreasing the amount of sludge wasted would be effective in increasing the mean cell residence time and providing a sludge with more desirable characteristics. This was not possible with Reactor 1, however, because sludge was not being wasted. In other words, the mean cell residence time was already as long as possible.

A sharp increase in effluent COD was also observed in Reactor 1; the COD increased from 178 mg/L on day 268 to 973 mg/L by day 288. Although original substrates were rarely detected in the effluent, its overall quality was no longer good. This change was also likely because of the low mean cell residence time. It appeared that using a synthetic waste with equal concentrations of each substrate, the maximum capacity of Reactor 1 operating

at an HRT of 1 day was about 400 mg/L of each substrate. Although an increase in HRT might have improved the reactor performance, this was not investigated since no real benefits would result. The reactor was terminated at day 288.

Before Reactor 1 experiments were completed, studies had also begun using Reactor 2. The original synthetic waste to this reactor contained (in addition to inorganic nutrients and minerals) about 300 mg/L acetone, 100 mg/L propionitrile, 40 mg/L pyrrole, and 400 mg/L thiocyanate. Based on Reactor 1 results, Reactor 2 was started using an HRT of 3 days. Sludge for the reactor was developed over several weeks by periodic feeding in a large batch reactor. Following 25 days of continuous flow operation, sampling began. The feed solution contained approximately 1370 mg/L COD, as shown in Figure 6-43. The 3-day HRT produced an effluent containing 66 mg/L COD. Original substrates were detected in the effluent only on day 26, when they were all below 4 mg/L. The reactor was operated under these conditions for a total of 35 days.

High effluent quality using an HRT of 3 days indicated that flow to Reactor 2 could be increased. An HRT of 2.5 days was selected and the reactor was operated at these conditions for 18 days. This change resulted in an average effluent COD of 53 mg/L and original substrates below 1 mg/L in the effluent. These results allowed the flow to be further increased to correspond to a 2-day HRT. Original substrates continued to be below the 1 mg/L detection limit in the effluent, which had an average COD of 48 mg/L. The reactor was operated at this flow rate for 24 days before increasing the flow so that the HRT would be 1.75 days. This flow produced an effluent with a COD of about 55 mg/L. Although original substrates were usually below 1 mg/L in the treated wastewater, occasional breakthroughs of up to 4 mg/L were observed, and two instances of 13 mg/L and 10 mg/L breakthroughs occurred. This HRT was held for 19 days.

The HRT was next reduced to 1.5 days. This flow rate was maintained for 11 days, during which time about 80 mg/L COD and original substrates below 2 mg/L were observed in the reactor effluent. The HRT was next decreased to 1.25 days. During 13 days of operation only one occurrence of an original substrate above 1 mg/L in the effluent was recorded, and effluent COD was an average of 85 mg/L. The HRT was then decreased to 1 day. This condition was maintained for 10 days and was characterized by an effluent containing an average of 83 mg/L COD and original substrates below 1 mg/L.

When a 1-day HRT continued to produce a high quality effluent, the feed strength was increased. Thiocyanate in the influent was increased to about 500 mg/L. Other substrate concentrations were unchanged because they already were very similar to those anticipated in a PFH wastewater. The concentration of thiocyanate, however, could be significantly higher (see Table 6-19). Since the objective of Reactor 2 operation was to treat a waste as close as possible to the actual expected wastewater, thiocyanate concentration was gradually increased.

Reactor 2 was fed the waste containing 500 mg/L thiocyanate for a total of 30 days at an HRT of 1 day. Original substrates were always below 2 mg/L in the effluent, which contained about 79 mg/L COD. Based on this result, thiocyanate in Reactor 2 was further increased to 600 mg/L, still using the 1-day HRT. At this point, thiocyanate gradually appeared in the effluent, approaching 250 mg/L. Other substrates remained under 1 mg/L in the effluent. COD of the treated wastewater was about 300 mg/L.

Figure 6-43. PERFORMANCE OF REACTOR 2

This result was not surprising since Neufeld, Mattson, and Lubon¹⁸ reported that substrate inhibition of thiocyanate degradation begins at thiocyanate concentrations of about 500 mg/L. The performance of Reactor 2 is in close agreement with the work of Neufeld et al. since the thiocyanate breakthrough in the effluent occurred abruptly when the influent concentration was increased above 500 mg/L. This cannot be considered a reactor failure since the only effluent COD increase is due to thiocyanate increase and since sludge color and settleability remained favorable.

To determine if additional reaction time would reduce the thiocyanate breakthrough, the HRT was increased to 1.5 days. Effluent COD remained near 300 mg/L, and thiocyanate continued to appear at concentrations of 200 to 250 mg/L. Feed to the reactor was then stopped until thiocyanate was completely degraded. The flow rate was resumed at a considerably slower pace to correspond to an HRT of 3 days.

It was at this point in the research that the Neufeld et al. study was located, which indicated that pH has a significant effect on thiocyanate metabolism. The concentration of the phosphate buffer in the influent was then increased by 50%. Potassium phosphate monobasic was also added to the reactor as necessary to maintain a reactor pH in the range of 6.7 to 7.2. Before this control, reactor pH was near 7.8.

The increase in HRT to 3 days did not initially appear to favorably affect thiocyanate removal. To test the ability of Reactor 2 to withstand an organic shock, the influent substrate concentrations were doubled for one day. This shock is seen on Figure 6-43 near Day 210. An increase in the thiocyanate effluent concentration from about 200 to 290 mg/L was observed within 3 days of the organic shock. The effluent COD approached 475 mg/L due to the thiocyanate level, since the other substrates continued to be below 1 mg/L in the effluent.

The Reactor 2 effluent thiocyanate concentration continued to be about 290 mg/L for four days and then began to decrease. The previous thiocyanate breakthrough of over 200 mg/L, however, was not reached as a steady-state concentration again. Within about one month of the organic shock, instead, thiocyanate concentrations of 1 to 4 mg/L were observed in the treated wastewater.

Thus, rather than the two or three HRT's one would expect for attainment of steady state, ten or eleven were required in this case. The performance of Reactor 2 illustrated the inability to predict the outcome of a treatability study and the importance of allowing ample time for a system to acclimate to a substrate, especially one for which substrate inhibition has been reported.

The virtual elimination of thiocyanate from the Reactor 2 effluent was not a function of HRT alone. Although the decline in effluent thiocyanate concentration followed an increase in HRT, it is likely the influence of HRT on other reactor parameters that actually caused the improved effluent quality. The increase in HRT, or decrease in flow, in turn, decreased the food to microorganism ratio in the aeration basin. The biological population was shifted to the right on the batch growth curve.

In effect, therefore, the increase in HRT also served to increase the mean cell residence time, which was likely the factor responsible for the improved thiocyanate treatment efficiency. Furthermore, the initiation of pH control served to optimize the reactor for thiocyanate metabolism and may have also contributed to the increased thiocyanate degradation efficiency.

When Reactor 2 reach the new steady-state effluent concentrations of 1 to 4 mg/L thiocyanate and about 115 mg/L COD, a second 1-day organic shock of twice the normal organic strength was administered. This shock, however, resulted in no observable deterioration of effluent quality. The thiocyanate effluent concentration, in fact, was below 1 mg/L, and average COD was about 100 mg/L. Thus, Reactor 2 performance continued to improve, even during an organically stressed condition.

Another organic shock, also shown in Figure 6-43, resulted in small perturbations in acetone and pyrrole in the effluent for 2 and 4 days, respectively, and a thiocyanate concentration of 1.1 mg/L for 1 day. A 2-day effluent COD increase to about 130 mg/L was observed, but COD then decreased to an average effluent level of 93 mg/L.

A one-way analysis of variance using the F test was performed on each of the effluent COD concentrations resulting from the three organic shocks and steady-state effluent COD. In each case, the difference in the mean COD of the treated wastewater resulting from the shock and the mean effluent COD during normal operation conditions was not statistically significant at the 0.05 level.

This discussion illustrates two important capabilities of the biological system. First, the unit became biologically acclimated to an influent thiocyanate concentration of about 600 mg/L, more than 100 mg/L greater than the concentration noted to cause substrate inhibition. Also, the capacity of the system to accept and overcome an organic shock was shown to be high. Changes in effluent quality observed following three 1-day periods of organic shock were not statistically significant at the 0.05 level.

Conclusions

The following conclusions can be drawn based on the results of experiments conducted by TTU during the project.

1. Acetone, propionitrile, pyrrole, and thiocyanate were shown to be biologically degradable in batch activated sludge experiments.
2. Batch reactors containing initial concentrations of 600, 300, or 100 mg/L of either acetone or propionitrile reached minimum COD levels of less than 30 mg/L within 50 hours of biological treatment.
3. Initial pyrrole concentrations of 600, 300, and 100 mg/L were biologically metabolized within 90 hours to COD residuals of less than 60 mg/L.
4. Batch experiments including 300, 100, and 50 mg/L thiocyanate as sole carbon sources revealed lag phases of 87 to 168 hours. About 100 additional hours of biological treatment were required to minimize the COD to 50 mg/L or less.

5. Double substrate experiments including pairs of acetone, propionitrile, and pyrrole showed that simultaneous metabolism of the pairs was possible in batch. Samples of the acetone-propionitrile experiment were analyzed using GC/MS, and no by-products other than carbon dioxide were detected.
6. Double substrate experiments including thiocyanate were characterized by immediate metabolism of one substrate and a lag in thiocyanate metabolism. This can not be considered sequential or preferential metabolism, since the same lag phase occurred with thiocyanate as the sole carbon source.
7. A continuous flow activated sludge unit (Reactor 1), which was fed 150 mg/L each of acetone, propionitrile, pyrrole, and thiocyanate was operated at HRT's as short as 1 day and consistently produced an effluent containing less than 1 mg/L each of original substrates and less than 70 mg/L COD.
8. When the organic strength of the feed to Reactor 1 was increased to as much as 400 mg/L each of acetone, propionitrile, pyrrole, and thiocyanate, breakthroughs of original substrates in the effluent were rare, and average effluent COD was less than 120 mg/L.
9. Reactor 1 failed when substrate concentrations were increased to 500 mg/L each. Although original substrates were less than 1 mg/L in the effluent, COD increased sharply, and sludge color, quantity, and settleability were unsatisfactory.
10. A second continuous flow reactor (Reactor 2) treated a synthetic wastewater containing 300 mg/L acetone, 100 mg/L propionitrile, 40 mg/L pyrrole, and 400 mg/L thiocyanate at HRT's as short as 1 day. Original substrates were below 1 mg/L in the reactor effluent, which exerted an average COD of less than 85 mg/L.
11. When the thiocyanate concentration in the Reactor 2 feed was increased to 500 mg/L, no change in effluent quality resulted at an HRT of 1 day.
12. An increase in the thiocyanate concentration to 600 mg/L in the Reactor 2 feed resulted in an effluent containing up to 250 mg/L thiocyanate. Reductions in flow to give HRT's of 1.5 and 3 days were not effective in improving effluent quality. These results were consistent with literature that reported substrate inhibition of thiocyanate metabolism beginning at influent thiocyanate concentrations of about 500 mg/L. However, the performance of the reactor improved with pH control and low COD values were again observed in the effluent.

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Subtask 6.2.2.b. Water Treatability Studies: Carbon Adsorption and Flocculation

Introduction

When shale is hydroretorted, water vapor generated from shale moisture and high-temperature water is in intimate contact with the oil and solid matrix at both high temperature and pressure.¹ As a result, numerous organic and inorganic constituents are present in the wastewater stream. Environmental data have been collected from a mini-bench scale unit using the PFH process. Table 6-21 shows the analyses of the wastewater from hydroretorting of three different Eastern oil shales.² Treatment of this wastewater stream is required prior to discharge and recycle.

The objective of this subtask was to determine the treatability of synthetic wastewaters comprised of acetone, propionitrile, pyrrole, thiocyanate and mixtures thereof by physical and chemical technologies. Specifically, removals of acetone, propionitrile, pyrrole, and thiocyanate by adsorption onto activated carbon and by chemical coagulation/precipitation with alum and ferric chloride were investigated.

Literature Review

The treatability of any compound by one of the various technologies available today is highly dependent on the properties of the compound. It is necessary, therefore, to examine some of the properties of acetone, propionitrile, pyrrole, and thiocyanate to determine if carbon adsorption or chemical coagulation/precipitation are feasible treatment alternatives. The properties of the compounds that are important in making this determination are the molecular weight, the solubility, the physical structure, and the polarity. The polarity of a molecule can be expressed by its dipole moment, which is the product of the distance separating charges of equal magnitude and opposite sign, times the magnitude of the charge. The greater the dipole moment, the greater is the polarity of the molecule.³ After a brief description of the properties for acetone, propionitrile, pyrrole, and thiocyanate, the relevant literature dealing with aspects of carbon adsorption and chemical coagulation/precipitation of these compounds is presented.

Properties of the Compounds

Acetone is a ketone containing three carbon atoms (C_3H_6O). It is a straight chain molecule with the ketone group attached to the second carbon atom. Acetone is a small molecule with a molecular weight of 58.08. Acetone is highly polar with a dipole moment of 2.88⁴ and is miscible in water.⁵

Propionitrile is similar to acetone in molecular weight (55.08) and structure. Like acetone, propionitrile is a straight-chain organic molecule containing three carbon atoms (C_3H_5N). Propionitrile has a nitrogen atom on the first carbon making it highly polar with a dipole moment of 3.56.⁴ The solubility of propionitrile at 40°C is 11.9 grams per 100 grams of water and at 100°C is 29 grams per 100 grams of water.⁶

Table 6-21. ANALYSES OF WASTEWATER FROM HYDRORETORTED EASTERN OIL SHALES

State Shale	Indiana New Albany	Tennessee Chattanooga	Alabama Chattanooga
<u>Element</u>	----- ppm -----		
Ag	0.6	0.6	0.9
Al	<5	6	<5
As	<0.5	1.1	2.2
Ba	<2	<2	<2
Ca	1	7	2
Cd	0.3	0.3	0.3
Cl	<10	<10	<10
Cr	0.5	0.7	0.5
Cu	5.3	3.7	1.8
Fe	7	2.9	16.8
Hg	1.5	3.1	2.5
K	3	4	6
Li	<1	<1	<1
Mg	1.7	1.5	1.7
Mn	0.3	0.5	0.7
Na	25	13	1.7
Ni	2	2	3
Pb	<2	<2	<2
Sb	<0.3	<0.3	<0.3
Se	<4	<4	<6
V	<2	<2	<2
Zn	7.3	9.4	7.4
<u>Sulfur Compounds</u>			
Thiocyanate	4850	7350	9400
Sulfide Sulfur	--	58,500	57,000
Sulfate Sulfur	2188	7150	4473
Total Sulfur	40,400	60,700	43,200
<u>Oxygenated Compounds</u>			
Methanol	20	BDL	NA
Ethanol	30	BDL	NA
Acetone	210	200	NA
MEK	90	50	NA
Pentanone	15	15	NA
Acetic Acid	200	BDL	NA
Propionic Acid	80	BDL	NA
Butanoic Acid	20	BDL	NA
Pentanoic Acid	20	BDL	NA
Hexanoic Acid	BDL	BDL	NA
Phenol	50	40	NA
Methyl Phenol	50	30	NA

Table 6-21, Cont. ANALYSES OF WASTEWATER FROM HYDRORETORTED
EASTERN OIL SHALES

State Shale	Indiana New Albany	Tennessee Chattanooga	Alabama Chattanooga
----- ppm -----			
<u>Nitrogen Compounds</u>			
Ammonia	32,900	42,700	31,400
Acetonitrile	440	360	NA
Propionitrile	60	40	NA
Aniline	170	500	NA
Methyl Anilines	75	180	NA
Pyrrole	200	130	NA
Methyl Pyrrole	190	70	NA
C ₂ -Pyrrole	60	15	NA
C ₃ -Pyrrole	15	BDL	NA
Pyridine	BDL	BDL	NA
Methyl Pyridines	15	30	NA
C ₂ -Pyridines	10	5	NA
C ₃ -Pyridines	30	BDL	NA
Cyanide	34	45	NA
<u>Hydrocarbons</u>			
Dihydroxybenzene	65	BDL	NA
Methyl Dihydroxybenzene	60	BDL	NA
C ₂ -Dihydroxybenzene	20	BDL	NA
<u>Miscellaneous Compounds</u>			
Fluorine	7	19	6
<u>Unidentified</u>	200	180	NA

NA = Not analyzed.

BDL = Below detectable limits.

The properties of pyrrole are different from those of acetone and propionitrile. It possesses a ring structure containing two double bonds as well as a nitrogen atom (C_4H_5N). It has a molecular weight of 67.09 and is the least polar of the four compounds with a dipole moment of 1.89.⁴ Pyrrole is sparingly soluble in water.⁵

Thiocyanate (SCN^-) differs from the other three compounds in that it is the only ionic species of the four. Thiocyanate contains one atom each of sulfur, carbon, and nitrogen, and its molecular weight is 58.08. Thiocyanate is very soluble in water.⁶

Carbon Adsorption

Tchobanoglous and Schroeder⁷ define adsorption as the accumulation of a material at the interface between two phases. Metcalf and Eddy⁸ similarly describe adsorption as the process of collecting soluble substances that are in solution on a suitable interface. In wastewater treatment applications, adsorption may be described as a partitioning process in which a contaminant is transferred from a dissolved state in the aqueous phase to the surface of a solid phase where it accumulates.⁹ The substance being removed from solution is referred to as the adsorbate while the solid phase onto which the substance accumulates is referred to as the adsorbent.¹⁰

Although several adsorbents are used for the process of adsorption, the one most commonly used for wastewater treatment is activated carbon.^{7,10-12} Activated carbon is an effective adsorbent because it is nonpolar and relatively inexpensive. (Polar adsorbents attract water and, therefore, would not be useful.)

Activated carbon is produced by exposing certain carbonaceous materials to three processes: dehydration, carbonization, and activation.¹² The carbonaceous materials used are generally coal, bone, wood, nut shells, or peat.^{7,8,10} Dehydration occurs by heating the materials at temperatures up to 170°C to remove excess water. Heating of the material is continued up to 400° to 600°C in the absence of air until it is reduced to a char. This process of carbonization causes decomposition of the material and drives off volatile substances. The final process, activation, involves treating the char with mixtures of carbon dioxide, air, and steam at temperatures of 750° to 950°C to remove amorphous residues (tars) from the pores formed during carbonization. Once these pores are cleaned and enlarged, the carbon possesses capacity for adsorption.¹²

The pores developed during activation may be classified according to size as follows: macropores, transitional pores, and micropores. The range of radii for macropores, transitional pores, and micropores are 5000 to 20,000, 40 to 200, and 18 to 20 angstroms, respectively.¹² Two measures of the pore sizes of activated carbons are the iodine number and the molasses number. The iodine number is a measure of pore sizes between 10 and 28 angstroms, while the molasses number is a measure of pore sizes greater than 28 angstroms. Carbons with a high iodine number would be suitable for adsorbing low molecular weight substances, while carbons with high molasses numbers would be suitable for high molecular weight substances.¹³

Activated carbon is marketed in powdered and granular forms. Virtually any sieve-size distribution of both forms can be obtained.⁷ In general, powdered activated carbon (PAC) is utilized when the adsorption process is carried out in batch systems, and granular activated carbon (GAC) is used when the adsorption process is carried out in continuous flow systems.

The adsorption process occurs in four steps: 1) the transport of the solute from the bulk solution phase to the boundary layer or surface film surrounding the adsorbent particle, 2) the transport of the solute across the boundary layer to the exterior surface of the adsorbent particle, 3) the diffusion of solute into the active pores of the adsorbent particle, and 4) the physical or chemical binding of the adsorbate to the internal surface of the adsorbent. The physical principle that describes the interactions between adsorbent and adsorbate is electrostatic attraction and repulsion. Other physical interactions include dipole-dipole interactions, van der Waals forces, and hydrogen bonding. Chemical adsorption is also based on electrostatic forces; however, the attraction between adsorbate and adsorbent approaches that of a covalent or electrostatic chemical bond between atoms, with shorter bond length and higher bond energy.¹⁰

The extent to which these physical or chemical phenomena cause a compound to be adsorbed varies from one compound to the other and is dependent on several factors. Snoeyink and Chen¹⁴ suggest that the most important factors affecting adsorption are the solubility, the molecular weight and the polarity of the adsorbate, and the pore size distribution of the adsorbent. In general, as the solubility and polarity of a compound increases, the extent of adsorption decreases, and as the molecular weight of a compound increases, the extent of adsorption increases. Further, pore sizes less than 70 angstroms are necessary to adsorb compounds with molecular weights less than 1000. Kutics *et al.*¹⁵ also emphasize the importance of pore size of the adsorbent and state that pore sizes of 10 angstroms (micropores) are necessary to adsorb low molecular weight compounds, such as acetone. The importance of solubility of the adsorbate is also discussed by Meardon *et al.*¹⁶ who state that carbon adsorption is not an effective process for removing organics that exhibit significant water solubility.

Another factor discussed by several authors that is important in determining the extent to which compounds are adsorbed by activated carbon is the pH of the wastewater solution. Randike¹⁷ suggests that adsorption increases as pH decreases. Martin and Iwugo¹⁸ state that adsorption will be strongest in the pH region that yields the highest proportion of undissociated molecules. It is also the contention of Snoeyink and Chen¹⁴ that adsorption increases as pH decreases.

The presence of other substances in solution with the compound of interest is also a factor in determining the extent to which a compound will be adsorbed. Fritz *et al.*¹⁹ simply point out that the presence of other compounds will affect the adsorption of each compound differently. Snoeyink and Chen state that the adsorption of a compound will only be decreased by the presence of another compound if one compound is very highly adsorbed. Otherwise, the presence of another compound will not affect the adsorption of the first compound. This was shown to be true for acetone by Annesini *et al.*²⁰ as will be discussed later. Godrej *et al.*²¹ suggest that analyzing these multicomponent systems by comparing the mole fraction adsorbed of each adsorbate is very beneficial.

Based on the properties of the compounds and the factors just discussed that affect the extent to which a compound is adsorbed, predictions can be made about the adsorption of acetone, propionitrile, pyrrole, and thiocyanate. Since all four compounds have low molecular weights, the extent of adsorption of each compound is expected to be relatively low. Pyrrole, having the highest molecular weight, the lowest degree of polarity, and the lowest solubility would be expected to be the most highly adsorbed of the four compounds. Acetone, propionitrile, and thiocyanate are very soluble, and acetone and propionitrile are also quite polar while thiocyanate is ionic. The molecular weights of acetone and thiocyanate are the same with the molecular weight of propionitrile being slightly less. On the basis of molecular weight, therefore, propionitrile would be expected to be least adsorbed since it has the lowest molecular weight; however, the difference in its molecular weight and the molecular weight of acetone and thiocyanate is very small. Because of its higher polarity, propionitrile should be adsorbed less than acetone as well, but on the basis of solubility, propionitrile should be the most adsorbed of these three compounds because it is the least soluble. The relative adsorbances of acetone and thiocyanate are not easily predicted because their molecular weights are identical, their solubilities are very high, and thiocyanate is ionic while acetone is not. Since water solubility is the most important factor in determining adsorption of soluble organics,¹⁶ it is predicted that propionitrile will be the second most adsorbed compound. Acetone and thiocyanate should be less adsorbed, and the ionic character of thiocyanate should affect its adsorption as well.

Only a few references are available that discuss the adsorption of these specific compounds onto activated carbon, with those for acetone being the most prominent. Forsythe *et al.*²² discuss the adsorption of acetone from a gaseous stream passing through a fixed bed, but do not deal with its removal from aqueous solution. Kutics *et al.* dealt with the adsorption of acetone from gaseous phase as well. Annesini *et al.*, however, discussed the adsorption of acetone from aqueous solution containing both single and multiple solutes. They report a relatively low removal of about 25 milligrams of acetone per gram of carbon at a final acetone concentration of 1162 mg/L from a single solute solution. The adsorption of acetone from three bi-solute solutions was then reported. In a binary system with methylisobutyl ketone, a highly adsorbed compound, a decrease in the adsorption of acetone was seen. In binary systems with propionaldehyde and sucrose, compounds not highly adsorbed, decreases in the adsorption of acetone could not be seen. These results support the statement by Snoeyink and Chen that adsorption of a compound from multiple solute solutions is decreased only if one of the compounds is highly adsorbed.

Osantowski and Hendriks²³ report that the average removal of thiocyanate by an activated carbon column was 79% from a water coming from a biological treatment process containing an average of 5 mg/L of thiocyanate. The only other reference dealing with the adsorption of these four compounds was by Prabhu *et al.*²⁴ at TTU. This reference reports the adsorption of acetone, propionitrile, pyrrole, and thiocyanate from single and multiple solute solutions containing greater than 100 mg/L of the compounds. The data reported by Prabhu *et al.* were combined with the data obtained from the experiments for this study with lower concentrations of the compounds to determine the adsorption of the compounds throughout a broad concentration range.

Results from carbon adsorption studies are generally reported in the form of isotherms. The three most commonly used isotherms are the Langmuir, the BET, and the Freundlich.^{8,10,12} The assumptions of the Langmuir isotherm are that the adsorbed layer will be one molecule thick, that all the adsorption sites have equal affinities for the adsorbate molecules, that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at adjacent sites, and that the adsorption is reversible and an equilibrium is reached. The BET isotherm is based on similar assumptions with the exception of an assumption that molecules can be adsorbed more than one layer thick on the surface of the adsorbent. The Freundlich isotherm is based on the assumption that the adsorbent has a heterogeneous surface with different classes of adsorption sites and also that the presence of adsorbed molecules on the adsorbent surface will affect the adsorption of the other adsorbate molecules.

The Langmuir and BET isotherms assume that the energy of adsorption is the same for all sites and not dependent on the degree of coverage. In reality, the energy of adsorption may vary because real surfaces are heterogeneous.¹⁰ The Freundlich isotherm attempts to account for this. This isotherm is the most widely used and is especially useful for data from multiple solute solutions.^{7,10,11} The Freundlich isotherm was used to analyze data for this study.

The form of the Freundlich isotherm is as follows:

$$X/M = KC^{1/n} \quad (6-13)$$

where X is the amount of solute adsorbed in milligrams, M is the weight of the adsorbent in grams, C is the concentration of solute remaining in solution after adsorption, and K and n are constants that vary with different solutes.¹² The Freundlich equation may be put in a useful form by taking the logarithm of both sides:

$$\log (X/M) = \log K + 1/n (\log C) \quad (6-14)$$

Data that yields a linear relationship when $\log (X/M)$ versus $\log C$ is plotted is said to be well represented by the Freundlich isotherm.

Chemical Coagulation/Precipitation

Chemical coagulation is the process of destabilizing colloidal particles.²⁵ By adding an appropriate floc-forming chemical reagent to a water or wastewater, nonsettleable colloidal solids are changed into a rapid-settling floc.²⁶ There are four major mechanisms involved in coagulation: 1) double layer compression, 2) charge neutralization, 3) enmeshment in a precipitate, and 4) interparticle bridging.^{25,27} Chemical precipitation, which is closely related to chemical coagulation, consists of the precipitation of unwanted ions from a water or wastewater.²⁶ During the process of chemical coagulation of wastewaters, precipitation can also occur.

Because acetone, propionitrile, pyrrole, and thiocyanate are soluble in water and do not form colloids, the process of coagulation would not be expected to remove these compounds based on its classical definition. Randike¹⁷ suggests that the colloidal destabilization mechanisms are not the

only mechanisms of coagulation. Randike, as well as Dempsey *et al.*,²⁸ suggest that the mechanisms of coagulation for the removal of soluble organic compounds are as follows: 1) adsorption of the organic compound onto the inorganic solids (floc) formed by the addition of the coagulant, 2) precipitation of the organic compound by its reaction with the coagulant, and 3) neutralization of charged sites on certain high molecular weight organic molecules causing them to curl up and stick to other molecules. Randike also states that the higher the molecular weight of the organic compound, the more likely it is to be removed by one of these mechanisms. Snoeyink and Chen also support the hypothesis that organic compounds may be removed by coagulation through two of the three mechanisms given above. They state that organic compounds may adsorb directly onto the floc that results from coagulant addition or they may be precipitated with coagulant metal ions and then removed.

Since the chemical coagulation/precipitation of acetone, propionitrile, pyrrole, and thiocyanate was not discussed in the literature, it was necessary to experimentally determine if the process was feasible. Based upon the mechanisms of removal of soluble organic compounds stated above, the compounds would only be expected to be removed by chemical coagulation/precipitation if they reacted to form a precipitate with the coagulant or if they were adsorbed onto floc formed by the coagulant.

The most widely used coagulants in water and wastewater treatment are aluminum sulfate (alum) and iron salts.²⁵⁻²⁷ When one of these chemicals is added to water, the hydrolyzing metal ions, Al(III) or Fe(III), are yielded and hydrate to form aquametal complexes.²⁷ These complexes go through a series of hydrolytic reactions to form a variety of soluble species that are very effective coagulants. Precipitation of metal hydroxides also occurs. The equilibria of these species is dependent on the pH of the solution.²⁷

The determination of the optimum pH and dosage of coagulant is made by conducting jar tests that vary these two parameters to determine the optimum conditions for coagulation.²⁵ TTU conducted the tests with both alum and ferric chloride to determine the removal of acetone, propionitrile, pyrrole, and thiocyanate by chemical coagulation/precipitation.

Methods and Materials

A discussion of the materials used and the methods followed in conducting the experiments for this study follows. The specific topics include Materials, Batch Experiments, Jar Tests, and Analytical Methods.

Materials

Batch carbon adsorption experiments were conducted using Filtrasorb 300 (F-300, Calgon Corporation) activated carbon. A sample of GAC was prepared for the tests by grinding in a ball mill and then sieving to collect the desired particle size. The fraction of this powdered activated carbon collected was -200+400 mesh. The collected fraction of powdered activated carbon was dried to constant weight at 105°C and stored in a dessicator until used. These procedures are the same as those reported by Dobbs and Cohen.²⁹

Two chemicals, aluminum sulfate and ferric chloride, were utilized in jar tests to determine the removals of acetone, propionitrile, pyrrole, and thiocyanate by chemical coagulation/precipitation. Stock solutions of these compounds were prepared in concentrations of 10 g/L and stored in the dark.

Synthetic wastewater solutions used for tests were prepared using distilled water and were stored at 4°C. All chemicals used in preparing the solutions were of reagent grade. All glassware was cleaned by soaking in chromic acid overnight, rinsing a minimum of five times with tap water, and oven drying at 105°C.

Batch Experiments

Batch experiments for determining the adsorption characteristics of the selected compounds onto activated carbon were conducted using light-resistant, ground-glass stoppered reagent bottles with volumes slightly greater than one liter as reactors. One liter volumes of the wastewater solutions were added to the reactors in concentrations ranging from 5 to 100 mg/L and stirred for four hours with a magnetic stirrer. To account for any decreases in concentrations that may have occurred due to adherence of the compounds to the sides of the glass, the solutions were then sampled to determine the initial solute concentration.

Following the four hours of stirring and sampling to determine the initial solute concentration, 1.25 grams of activated carbon were thoroughly wetted using 50 ml of distilled water and added to the reactors. This solution was stirred for four additional hours to allow equilibrium to be reached. This differs from the procedure reported by Dobbs and Cohen in which only two hours of contact time were permitted for adsorption.²⁹ Two hours allowed more than 90% of equilibrium to be reached; however, the authors indicated that a four-hour contact time would result in greater capacities and would be preferable in some applications.²⁹

After four hours of contact time between the carbon and wastewater solutions, samples were collected, filtered through 0.2 micron filter paper, and the final solute concentrations determined. These data were tabulated and used to develop adsorption isotherms.

In determining the adsorption of the four selected compounds onto activated carbon, three series of batch experiments were conducted. The first series was with single solute solutions. The purpose of these experiments was to determine the adsorptive capacity of activated carbon for the four selected compounds. The second series of experiments was with synthetic wastewater solutions containing all four compounds -- multiple solute solutions. The purpose of this series of experiments was to determine the effect of multiple solutes on the adsorption of single solutes. These two series of experiments determined the suitability of activated carbon as a primary treatment process.

The third and final series of experiments were conducted with effluent from a small-scale continuous flow biological reactor that was being fed a synthetic wastewater solution containing all four compounds. The purpose of these tests was to determine if carbon adsorption would be a suitable polishing process following biological treatment of these compounds if it was not used as a primary treatment technique. Because the original four

compounds were not detectable in the effluent and breakthrough of these compounds might occur in an actual system, it was spiked with the four compounds and then used in this series of experiments. By spiking the effluent with acetone, propionitrile, pyrrole, and thiocyanate, not only was the reduction of COD from biological endproducts generated by the breakdown of the compounds determined, but the removals of the original four compounds from biological effluent was also determined.

In this series of batch carbon adsorption experiments, it was necessary to slightly modify the experimental procedure used with the synthetic wastewater solutions. The effluent from the biological reactor was coagulated with alum at a concentration of 200 mg/L to remove suspended particulates and minimize the number of microorganisms present, and then the solutions were spiked with 100 mg/L each of acetone, propionitrile, pyrrole, and thiocyanate. Quantities of activated carbon ranging from 0.5 grams to 2.0 grams were then added to the reactors. The initial solutions were prepared by collecting about twelve liters of the biological effluent and coagulating and spiking the entire solution. This insured uniform distribution and concentrations of biological endproducts in all reactors.

Jar Tests

Jar tests for determining the removals of the four compounds by chemical coagulation/precipitation were conducted in one-liter beakers on a standard six paddle stirrer (Phipps & Bird, Inc.) jar test machine. One-liter volumes of the wastewater solutions were added to the beakers with each having the same concentrations of all four compounds. Dosages of a coagulant (alum or ferric chloride) were added to the beakers, and these solutions were stirred for one minute at 100 rpm of the stirring arm. Agglomeration of the floc particles was enhanced by stirring the solutions for five minutes at 30 rpm and then five additional minutes at 5 rpm. Following stirring, the floc was allowed to settle for 15 minutes. Samples were then taken from the clear supernatant, filtered through 0.2-micron filter paper, and the final concentrations of acetone, propionitrile, pyrrole, and thiocyanate were measured.

In determining the removals of the four compounds by chemical coagulation/precipitation, two series of jar tests were conducted for each coagulant. In the first series of jar tests with ferric chloride, the pH was held at 6 (an average pH for the wastewater stream) with sodium hydroxide, and coagulant additions were varied from 0 to 200 mg/L. The coagulant addition that proved to be optimum in these tests was held constant in the second series of tests with ferric chloride, while the pH of the waste solutions was varied from 5 to 11. If removal of the compounds by chemical coagulation/precipitation had been successful, a series of tests with varying dosages would have been performed at all pH values since optimum dosage can change with different pH values. The initial concentration of solutes in both series of tests was 100 mg/L of each compound.

Similarly, the first series of jar tests with alum was conducted with constant pH and different coagulant dosages, while the second series was conducted with constant coagulant dosages and different pH values. In the first series of jar tests with alum, the pH was held at 7 and coagulant additions were varied from 0 to 600 mg/L. The coagulant dosage that proved to

be optimum in these tests was held constant in the second series of jar tests with alum and the pH of the waste solution was varied from 3 to 11. Different pH values and coagulant dosages were used for the two coagulants to produce flocs that were similar in quality and quantity. As with ferric chloride, the initial concentration of solutes in both series of tests with alum was 100 mg/L of each compound.

Analytical Procedures

The analyses of samples from batch carbon adsorption experiments and jar tests with synthetic wastewater solutions involved two procedures. First, the concentrations of acetone, propionitrile, and pyrrole were determined using a Hewlett-Packard Model 5890A Gas Chromatograph (GC). The column used was 6-feet (1.83 m) long and 1/4-inch (6.4-mm) outside diameter and packed with 60/80 Carbowpack B/l percent SP-1000 supplied by Supelco.³⁰ By programming the GC to have an initial time and temperature of 1 minute and 80°C, a rate of 20°C per minute, and a final time and temperature of 3.5 minutes and 150°C, the peaks for acetone, propionitrile, and pyrrole were seen at 1.8, 2.4, and 6.6 minutes, respectively. Second, the concentrations of thiocyanate were determined by a colorimetric procedure for cyanides amenable to chlorination.³¹ Adsorbances for these colorimetric analyses were measured using a Perkin-Elmer Lambda 3 UV-Visible Spectrophotometer.

The analyses of samples taken from the third series of batch carbon adsorption experiments (those with biological effluent) utilized the GC and the colorimetric procedure described above as well as the measurement of COD generated from the biological endproducts in the effluent. COD was measured using the closed reflux, colorimetric method.³¹ All samples that were collected were stored in a refrigerator and analyzed as soon as possible. The maximum storage time permitted was one week; however, most samples were analyzed within one or two days.

Results and Discussion

The results from the carbon adsorption and coagulation experiments are discussed below. Subsections for the carbon adsorption experiments include those for acetone, propionitrile, pyrrole, and thiocyanate as well as a subsection that quantitatively compares the relative adsorbances of the four compounds onto activated carbon. The results from the coagulation experiments are broken into subsections for ferric chloride and alum. The performance of the two coagulants is compared as well.

Carbon Adsorption

The results from batch carbon adsorption experiments with both synthetic waste solutions and effluent from a continuous flow biological reactor that was fed a synthetic waste solution of acetone, propionitrile, pyrrole, and thiocyanate are presented below. The data shown for final concentrations less than 100 mg/L were obtained experimentally, while the data for higher final concentrations was obtained from previous TTU experiments.²⁴

Acetone

The results for the adsorption of acetone onto activated carbon from single and multiple solute solutions of synthetic wastewater are shown in Figures 6-44 through 6-46. Figure 6-44 shows the Freundlich isotherm for single solute experiments, Figure 6-45 shows the Freundlich isotherm for multiple solute experiments, and Figure 6-46 shows the superposition of these two isotherms. These figures illustrate that the Freundlich isotherm represents the data quite well; however, some scatter of data is evident. These three figures also illustrate that acetone has a relatively low affinity for activated carbon with only about 40 milligrams of acetone removed per gram of carbon at a final concentration of 1100 mg/L and about 4 milligrams removed per gram of carbon at a final concentration of 1 mg/L. Compounds with very high affinities for activated carbon will demonstrate removals of several thousand milligrams per gram of carbon such as bis-(2-ethylhexyl) phthalate, which has an X/M value of 11,300 mg/g at a final concentration of 1 mg/L.²⁹ These values are slightly greater than those reported by Annesini *et al.*²⁰ who give a removal of about 25 milligrams of acetone per gram of carbon at a final concentration of 1162 mg/L. This low affinity of acetone for activated carbon was expected because acetone has a low molecular weight, a high solubility, and is highly polar.

Figure 6-46 shows that the adsorption of acetone in single and multiple solute experiments is similar. This is due to the low affinity of acetone for activated carbon as well as the relatively low affinities of all the compounds for activated carbon when compared to other compounds. This supports the statement by Snoeyink and Chen that the adsorption of a compound will only be decreased by the presence of other compounds if one of the compounds is very highly adsorbed. A possible explanation of this is that with so little acetone being adsorbed, all of the active sites on the carbon were not filled, thus the presence of other compounds that were not highly adsorbed had little effect on the adsorption of acetone. If larger quantities of acetone had been adsorbed from single solute solutions, or if the other compounds were highly adsorbed, the presence of multiple solutes would have been expected to decrease the adsorption of acetone. The data shown in Figure 6-46, however, makes it almost impossible to differentiate the adsorption of acetone from single and multiple solute solutions.

Figure 6-47 shows the results from an equilibrium experiment conducted to ensure that the four-hour contact between activated carbon and acetone was sufficient for equilibrium to be reached. The data shown in Figure 6-47 illustrates that for a solution with an initial concentration of about 9 mg/L of acetone, the four-hour contact time was more than adequate for equilibrium to be reached. Similar results were obtained for solutions with higher concentrations; this figure is shown to illustrate typical results.

Batch carbon adsorption experiments with spiked effluent from a continuous-flow biological reactor being fed all four compounds were also conducted. The initial COD of the effluent was 40 mg/L and residual concentrations of acetone, propionitrile, pyrrole, and thiocyanate were below detectable limits (less than 1 mg/L). Table 6-22 shows that this initial COD (generated from the presence of biological endproducts) could be reduced to about 25 mg/L at all of the carbon additions used. Thus, about 15 mg/L of the COD reduction in the experiments with spiked biological effluent can be

Figure 6-44. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF ACETONE FROM A SINGLE SOLUTE SOLUTION

Figure 6-45. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF ACETONE FROM A MULTIPLE SOLUTE SOLUTION

Figure 6-46. FREUNDLICH ISOTHERMS FOR THE ADSORPTION OF ACETONE FROM SINGLE AND MULTIPLE SOLUTE SOLUTIONS

Figure 6-47. EQUILIBRIUM EXPERIMENT RESULTS FOR THE ADSORPTION OF ACETONE

Table 6-22. REDUCTION OF COD IN THE EFFLUENT FROM A CONTINUOUS FLOW BIOLOGICAL REACTOR BY ACTIVATED CARBON

<u>Carbon Dosage,</u> <u>g/L</u>	<u>Final COD,</u> <u>mg/L</u>
0.0	40
0.5	23
1.0	26
1.5	23
2.0	26

attributed to removal of the biological endproducts that were present initially. The remainder of the COD reduction in the experiments with spiked effluent would then be attributed to the removals of the four compounds.

Table 6-23 shows the removals of each of the four compounds from the spiked biological effluent. Increasing carbon additions resulted in increased removals of the compounds. Table 6-24 shows those results for acetone in the form of Freundlich isotherm coordinates. The values of X/M are similar to the values plotted in Figure 6-46 in the same final concentration range. These results show that acetone has a low affinity for activated carbon and that the presence of the other four compounds did not affect the adsorption of acetone. Neither did the presence of the initial 40 mg/L of COD from the biological endproducts decrease the amount of acetone adsorbed.

Table 6-23. REMOVALS OF ACETONE, PROPIONITRILE, PYRROLE, AND THIOCYANATE BY ACTIVATED CARBON FROM BIOLOGICAL EFFLUENT SPIKED WITH 100 mg/L OF EACH COMPOUND

<u>Carbon Dosage,</u> <u>mg/L</u>	<u>Final Acetone,</u> <u>mg/L</u>	<u>Final Propionitrile,</u> <u>mg/L</u>	<u>Final Pyrrole,</u> <u>mg/L</u>	<u>Final Thiocyanate,</u> <u>mg/L</u>
0.0	96.1	91.9	87.9	93.1
0.5	90.3	85.3	73.9	89.7
1.0	87.6	81.2	60.3	86.3
1.5	85.4	78.8	49.1	83.2
2.0	82.7	75.9	39.8	80.3

Table 6-24. REMOVALS OF ACETONE REPORTED IN MILLIGRAMS PER GRAM OF CARBON (From Table 6-23)

<u>Final Concentration,</u> <u>mg/L</u>	<u>Milligrams Acetone Removed</u> <u>per Gram of Carbon</u>
90.3	10.6
87.6	8.5
85.4	7.2
82.7	6.7

Propionitrile

Figures 6-48 through 6-50 show the results for the adsorption of propionitrile onto activated carbon from single and multiple solute solutions of synthetic wastewater. The Freundlich isotherm for single solute experiments is shown in Figure 6-48, the Freundlich isotherm for multiple solute experiments is shown in Figure 6-49, and the two isotherms are superimposed in Figure 6-50. The results from single solute experiments fit the Freundlich isotherm very well as shown in Figure 6-48, but some scatter of data was observed in Figure 6-49 for the results from multiple solute experiments.

Propionitrile exhibited a higher affinity for activated carbon than did acetone as predicted from its lower solubility. This property seemed to be more important than polarity or molecular weight since the propionitrile molecule is more polar and slightly smaller than the acetone molecule but still more highly adsorbed. The adsorption of propionitrile in single solute experiments ranged from 0.5 to 223 milligrams per gram of carbon within a final concentration range of 3 to 1200 mg/L, while the adsorption of propionitrile in multiple solute experiments ranged from 1 to 28 milligrams per gram of carbon within a final concentration range of 3 to 700 mg/L. Data for higher final concentrations of propionitrile in multiple solute experiments was not given in the literature; however, a good comparison of the data is still possible.

Figure 6-50 demonstrates that at final concentrations below 10 mg/L, there is very little difference in the adsorption of propionitrile from single and multiple solute solutions; however, at final concentrations of propionitrile greater than 10 mg/L, the adsorption of propionitrile is slightly decreased by the presence of the other compounds. As the competition for active sites increased in the multiple solute solutions, the amount of propionitrile adsorbed was slightly less than that from single solute solutions. Even though propionitrile was not highly adsorbed relative to other compounds, the adsorption of propionitrile was high enough to experience interference from the presence of other compounds. This trend would continue with increasing concentrations and numbers of solutes.

The results from an equilibrium experiment with propionitrile are shown in Figure 6-51. The data illustrate that for a solution with an initial concentration of about 9 mg/L, a four-hour contact time was more than sufficient for equilibrium to be reached between propionitrile and activated carbon.

Table 6-25 shows the removals of propionitrile from spiked biological effluent reported in Table 6-23. These values of X/M compare favorably with those for the multiple solute experiments shown in Figure 6-49. The similarity of values indicates that propionitrile could still be adsorbed from biological effluent and that the biological endproducts did not adversely affect its degree of adsorption. The affinity of propionitrile for activated carbon was high enough to see interference in its adsorption from a multiple solute solution, but the affinity of this compound for activated carbon was not great enough for a difference to be detected between adsorption from multiple solute solutions of synthetic waste and multiple solute solutions of biological effluent containing an additional 40 mg/L of COD from biological endproducts.

Figure 6-48. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF PROPIONITRILE FROM A SINGLE SOLUTE SOLUTION

Figure 6-49. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF PROPIONITRILE FROM A MULTIPLE SOLUTE SOLUTION

Figure 6-50. FREUNDLICH ISOTHERMS FOR THE ADSORPTION OF PROPIONITRILE FROM SINGLE AND MULTIPLE SOLUTE SOLUTIONS

Figure 6-51. EQUILIBRIUM EXPERIMENT RESULTS FOR THE ADSORPTION OF PROPIONITRILE

Table 6-25. REMOVALS OF PROPIONITRILE REPORTED IN
MILLIGRAMS PER GRAM OF CARBON (From Table 6-23)

Final Concentration, mg/L	Milligrams Propionitrile Removed per Gram of Carbon
85.3	13.2
81.2	10.7
78.8	8.8
75.9	8.0

Pyrrole

The results for the adsorption of pyrrole onto activated carbon from synthetic wastewater solutions are shown in Figures 6-52 through 6-54. Figure 6-52 shows the Freundlich isotherm for single solute experiments, Figure 6-53 shows the Freundlich isotherm for multiple solute experiments, and Figure 6-54 shows the superposition of the two isotherms. The data for these experiments are well represented by the Freundlich isotherm as evidenced by all three figures. The values of X/M demonstrate that pyrrole had the highest affinity for activated carbon of the four compounds. Higher values of X/M are seen on the isotherms for propionitrile, but only at final concentrations higher than those shown for pyrrole. By comparing X/M ratios for propionitrile and pyrrole at the same final concentrations, the higher affinity of pyrrole for activated carbon is seen. The high affinity of pyrrole for activated carbon was expected based on its highest molecular weight, lowest polarity, and lowest solubility of the four compounds.

Figure 6-54 demonstrates that the adsorption of pyrrole from multiple solute solutions was consistently less than that from single solute solutions. Even though pyrrole's affinity for activated carbon was not in the very high range exhibited by some compounds, it was high enough for adsorption to be decreased in the presence of other compounds. This same trend was observed with propionitrile for final concentrations greater than 10 mg/L, but was not observed for acetone. Because such a relatively small amount of acetone was adsorbed, a difference could not be made between the results from single and multiple solute solutions. With propionitrile and pyrrole, however, adsorption is high enough to see the interference from the presence of other compounds.

Figure 6-55 shows the results from an equilibrium experiment with pyrrole to determine if the four-hour contact time was sufficient for equilibrium to be reached between pyrrole and activated carbon. As with acetone and propionitrile, the four-hour contact period was much more than necessary for equilibrium to be reached in a solution containing about 9 mg/L of pyrrole initially. The same was true for higher initial concentrations of pyrrole as well.

The removal of pyrrole from the spiked biological effluent was shown in Table 6-23. Those values are shown in Table 6-26 in the form of Freundlich isotherm coordinates. The values of X/M are very similar to those obtained for pyrrole in multiple solute experiments in the same final concentration range seen in Figure 6-53. This indicates that the presence of the biological

Figure 6-52. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF PYRROLE FROM A SINGLE SOLUTE SOLUTION

Figure 6-53. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF PYRROLE FROM A MULTIPLE SOLUTE SOLUTION

Figure 6-54. FREUNDLICH ISOTHERMS FOR THE ADSORPTION OF PYRROLE FROM SINGLE AND MULTIPLE SOLUTE SOLUTIONS

Figure 6-55. EQUILIBRIUM EXPERIMENT RESULTS FOR THE ADSORPTION OF PYRROLE

Table 6-26. REMOVALS OF PYRROLE REPORTED IN
MILLIGRAMS PER GRAM OF CARBON (From Table 6-23)

<u>Final Concentration,</u> <u>mg/L</u>	<u>Milligrams Propionitrile Removed</u> <u>per Gram of Carbon</u>
73.9	28.1
60.3	27.6
49.1	25.9
39.8	24.1

endproducts did not inhibit the adsorption of pyrrole from multiple solute solutions. Recall that a difference in the adsorption of propionitrile from single and multiple solute solutions could be seen while a difference in adsorption could not be seen with the additional 40 mg/L of COD from biological endproducts. Similarly, a difference in the adsorption of pyrrole from single and multiple solute solutions could be seen while a difference in adsorption from biological effluent spiked with all four compounds was not evident.

Thiocyanate

Figures 6-56 through 6-58 show the results for the adsorption of thiocyanate onto activated carbon from single and multiple solute solutions of synthetic wastewater. The Freundlich isotherm for single solute experiments is shown in Figure 6-56, the Freundlich isotherm for multiple solute experiments is shown in Figure 6-57, and the two isotherms are superimposed in Figure 6-58. A very low affinity of thiocyanate for activated carbon is evidenced by a maximum value of 24 mg of thiocyanate removed per gram of activated carbon at a final concentration of 655 mg/L from a single solute solution. Thus, thiocyanate had the lowest affinity for activated carbon of the four compounds.

As with acetone, the low affinity of thiocyanate for activated carbon makes differentiating the removals of thiocyanate from single and multiple solute solutions very difficult. The linear least squares fit, however, shows that at concentrations greater than 20 mg/L, the presence of the other compounds in multiple solute solutions decreases the amount of thiocyanate adsorbed.

A possible explanation for this interference may be seen by examining the equilibrium experiment for thiocyanate (Figure 6-59). As with the other three compounds, a four-hour contact time was more than sufficient for equilibrium to be reached between thiocyanate and activated carbon. However, three hours was necessary for thiocyanate to reach equilibrium with the carbon where only 15 to 30 minutes was necessary for the other three compounds to reach equilibrium. Perhaps thiocyanate adsorption showed a decrease in multiple solute experiments even though its affinity for carbon was very low because its rate of adsorption was slower than the three other compounds. The behavior of acetone, propionitrile, and pyrrole was determined to be quite similar. With thiocyanate, however, the rate of adsorption is slower. Thus deviations in the behaviour of thiocyanate from that of the other compounds are not unlikely.

Figure 6-56. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF THIOCYANATE FROM A SINGLE SOLUTE SOLUTION

Figure 6-57. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF THIOCYANATE FROM A MULTIPLE SOLUTE SOLUTION

Figure 6-58. FREUNDLICH ISOTHERMS FOR THE ADSORPTION OF THIOCYANATE FROM SINGLE AND MULTIPLE SOLUTE SOLUTIONS

Figure 6-59. EQUILIBRIUM EXPERIMENT RESULTS FOR THE ADSORPTION OF THIOCYANATE

Table 6-27 shows the results for thiocyanate from the experiments with spiked biological effluent in the form of Freundlich isotherm coordinates. The values of X/M are similar to those for multiple solute experiments in the same range of final concentrations. This is reasonable, based on the results seen for the other three compounds. Neither acetone, propionitrile, nor pyrrole had an affinity high enough for activated carbon to show a difference in adsorption from multiple solute solutions of synthetic wastewater and multiple solute solutions of biological effluent containing the additional 40 mg/L of COD. The low adsorption of thiocyanate and the reliability of the analytical method make the removals from multiple solute solutions and from spiked biological effluent indistinguishable. As discussed earlier, the rate of adsorption could have contributed to reduced adsorption of thiocyanate in the presence of multiple solutes.

Table 6-27. REMOVALS OF THIOCYANATE REPORTED IN
MILLIGRAMS PER GRAM OF CARBON (From Table 6-23)

<u>Final Concentration,</u> <u>mg/L</u>	<u>Milligrams Propionitrile Removed</u> <u>per Gram of Carbon</u>
89.7	6.9
86.3	6.8
83.2	6.6
80.3	6.4

Based on polarity, solubility, and molecular weight, pyrrole was predicted to be the most highly adsorbed and that propionitrile would be second most highly adsorbed, and these predictions proved to be correct. This also illustrated that solubility was more important than polarity and molecular weight in determining the affinity of a compound for activated carbon. Because acetone and thiocyanate have identical molecular weights and are highly soluble, the relative affinities of the two could not be predicted except to say that their adsorptions would be less than those of pyrrole and propionitrile. The experimental data showed that thiocyanate was the least preferred of the four compounds with acetone having the third highest affinity for activated carbon.

Quantitative Comparisons

In previous sections, comparisons were made for each compound between its adsorption from single and multiple solute synthetic waste solutions as well as from spiked biological effluent. Comparisons of the relative adsorbances of the compounds have also been made and the compounds have been ranked in order of highest to lowest affinity. It is important, however, to quantify these relationships to determine the relative quantities of each compound adsorbed from multiple solute solutions. This can be done by determining the average mole fraction of each compound adsorbed from the multiple solute solutions. The following relationship is used:

$$Z_i = q_i/q_t \quad (6-15)$$

where Z_i is the mole fraction of compound i adsorbed onto carbon, q_i is the moles of compound i adsorbed, and q_t is the total moles of all compounds

adsorbed in a given experiment, thus q_t is the total mass loading of the carbon in moles.

The value of Z_i can be calculated from data for multiple solute experiments to determine if there is a preference for adsorption of any of the compounds over the others. The values of Z_i obtained for acetone, propionitrile, pyrrole, and thiocyanate from experiments conducted with multiple solute solutions were 0.17, 0.23, 0.49, and 0.11, respectively. This indicates that pyrrole was the most preferred compound for adsorption followed by propionitrile, acetone, and thiocyanate. These relationships agree with the rankings made based on the isotherms that were obtained for the compounds.

The quantities of acetone, propionitrile, pyrrole, and thiocyanate adsorbed per gram of carbon were small relative to compounds for which thousands of milligrams can be adsorbed onto a gram of carbon. To be sure that these low adsorbances were due to low affinities of the compounds for activated carbon and not to a poor quality activated carbon, two experiments were conducted to determine if the carbon was of good quality. The first was to reproduce data which were published for the adsorption of a compound onto Filtrasorb 300 activated carbon. The compound selected was benzene. Figure 6-60 shows both the line for the isotherm published by EPA³² for the adsorption of benzene onto activated carbon as well as the experimental data that were obtained from the adsorption of benzene onto the same batch of Filtrasorb 300 used in experiments with acetone, propionitrile, pyrrole, and thiocyanate. The results obtained are very similar to those published by EPA; in fact, the adsorption of benzene onto Filtrasorb 300 as determined experimentally was slightly greater than the adsorption published by EPA. These results indicate that the activated carbon used for these studies was of acceptable quality and that the low adsorbances of acetone, propionitrile, pyrrole, and thiocyanate were in fact due to their low affinities for activated carbon.

The second experiment was the determination of the carbon iodine number. The iodine number of an activated carbon refers to the milligrams of iodine adsorbed during a standard test.³³ It is a measure of the volume present in pores from 10 to 28 angstroms in diameter. Activated carbons with a high percentage of pore sizes in this range would be suitable for adsorbing low molecular weight substances such as those in this study. Typical powdered activated carbons have iodine numbers of 800 ± 100 . The iodine number for the Filtrasorb 300 being utilized was determined to be 1074 by the standard procedure referenced above. This indicates that not only was the carbon of good quality, but that the carbon would also be very suitable for adsorbing low molecular weight compounds such as the four compounds under investigation. These results, as well as those for the adsorption of benzene, indicated that the activated carbon was of good quality and highly suitable for these compounds.

A final set of experiments was conducted to try to increase the adsorption of the four compounds onto activated carbon by changing the chemical conditions of the experiments. Those experiments were batch carbon adsorption experiments using multiple solute synthetic waste solutions with varying pH. As noted earlier, several authors had stated that adsorption increases as pH decreases. The results shown thus far for batch carbon adsorption experiments were conducted in solutions with a pH of 6. The final

Figure 6-60. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF BENZENE ONTO FILTRASORB 300

set of experiments was conducted with synthetic waste solutions containing 100 mg/L of each compound and pH values ranging from 3.1 to 10.5. Table 6-28 shows the quantity of each compound removed per gram of carbon at each of the pH values. As expected, at pH values above 6, adsorption of the compounds was decreased, while at pH values less than 6, adsorption of the four compounds was increased. The increased quantities adsorbed, however, only ranged from 3 to 6 milligrams per gram of carbon for the four compounds. Thus the affinities of the compounds for activated carbon seen in the experimental results could not be significantly increased by adjusting the pH of the waste solutions.

Table 6-28. QUANTITIES OF ACETONE, PROPIONITRILE, PYRROLE, AND THIOCYANATE REMOVED BY ADSORPTION ONTO ACTIVATED CARBON AT VARYING pH VALUES

<u>pH</u>	<u>Acetone</u>	<u>Propionitrile</u>	<u>Pyrrole</u>	<u>Thiocyanate</u>
	----- mg Removed/g Carbon -----			
3.1	15.5	16.7	41.5	13.5
4.0	14.5	15.1	37.1	13.0
6.0	12.1	12.8	35.1	10.7
7.8	9.7	10.5	32.5	8.4
9.3	8.3	8.7	28.4	7.9
10.5	6.9	6.6	27.2	7.5

Chemical Coagulation/Precipitation

The results from the coagulation experiments (jar tests) with acetone, propionitrile, pyrrole, and thiocyanate are presented below.

Ferric Chloride

Figure 6-61 shows the results from jar tests conducted while maintaining a pH of 6 with sodium hydroxide and varying additions of ferric chloride from 0 to 200 mg/L. The initial concentrations of acetone, propionitrile, pyrrole, and thiocyanate were 99.3, 97.2, 105.3, and 111.1 mg/L, respectively. Removals of the compounds increased with increasing coagulant addition up to 100 mg/L. At additions of ferric chloride greater than 100 mg/L, removals of the four compounds remained fairly constant. The maximum removals observed for acetone, propionitrile, and pyrrole were about 20 mg/L while 13 mg/L of thiocyanate was removed.

The amount of floc formed at 100 mg/L was about 100 mL in volume following sedimentation in the jar test procedure. This volume of floc was not significantly increased with higher coagulant dosages; instead, the solutions became slightly orange indicating an iron compound in solution. Thus, it is concluded that the removals of the four compounds were a result of adsorption of the compounds onto the floc as described by Snoeyink and Chen because an increase in the quantity of floc with increasing coagulant dosage up to 100 mg/L corresponded to an increase in removals of the compounds.

Using a ferric chloride addition of 100 mg/L, jar tests were conducted to determine the effect of pH on the removals of acetone, propionitrile, pyrrole, and thiocyanate. The results, (Figure 6-62) show maximum removals were

Figure 6-61. REMOVAL OF ACETONE, PROPIONITRILE, PYRROLE, AND THIOCYANATE BY CHEMICAL COAGULATION/PRECIPITATION WITH FERRIC CHLORIDE

Figure 6-62. REMOVAL OF ACETONE, PROPIONITRILE, PYRROLE, AND THIOCYANATE BY CHEMICAL COAGULATION/PRECIPITATION WITH 100 mg/L FERRIC CHLORIDE

Figure 6-60. FREUNDLICH ISOTHERM FOR THE ADSORPTION OF BENZENE ONTO FILTRASORB 300

Figure 6-63. REMOVAL OF ACETONE, PROPIONITRILE, PYRROLE, AND THIOCYANATE BY CHEMICAL COAGULATION/PRECIPITATION WITH ALUM

unrelated to pH. Removals of the four compounds at all pH values were low with removals of acetone, propionitrile, and pyrrole being about 20 mg/L and removals of thiocyanate ranging from 10 to 17 mg/L. If one pH value was to be selected as superior, it would be a pH of 9 where removals of all four compounds were slightly greater than at the other pH values.

Alum

The results from jar tests conducted at a pH of 7 with alum additions ranging from 0 to 600 mg/L are shown in Figure C-63. Removals of the acetone, propionitrile, and pyrrole were proportional to alum addition up to 500 mg/L, while removals of thiocyanate did not increase at alum concentrations greater than 100 mg/L. At a concentration of 500 mg/L, removals of about 15 mg/L were observed for acetone, propionitrile, and pyrrole while removals of about 30 mg/L were observed for thiocyanate at concentrations of 100 mg/L and greater.

The volume of floc formed at an alum addition of 500 mg/L was about 100 ml following sedimentation. No observable change in the volume of floc was seen at an alum addition of 600 mg/L. It is concluded that the removals of acetone, propionitrile, and pyrrole were a result of adsorption onto the floc, because when the volume of floc increased with increasing alum addition up to 500 mg/L, the removals of these three compounds also increased. It is also concluded, however, that the removal of thiocyanate by alum may have been by a mechanism other than adsorption onto the floc because removals did not increase at alum additions greater than 100 mg/L even though floc volumes did. It is also interesting to note that the removals of acetone, propionitrile, and pyrrole with 100 mg/L of ferric chloride were very similar to their removals with 500 mg/L of alum. These two coagulant additions yielded similar volumes of floc, and thus similar reductions in concentrations of acetone, propionitrile, and pyrrole, further indicating removals of these compounds by adsorption onto the floc.

Figure 6-64 shows the results from jar tests conducted to determine the removals of the four compounds as a function of pH. The alum concentration used was 500 mg/L, and the initial concentrations of acetone, propionitrile, pyrrole, and thiocyanate were 97.2, 96.4, 96.7, and 99.5 mg/L, respectively. The results (Figure 6-64) show that the removals of the compounds were greatest at a neutral pH, while decreased removals were observed at higher and lower pH values. Maximum removals of about 23 mg/L were observed at a pH of 6.5 for acetone, propionitrile, and pyrrole, while a maximum removal of 32 mg/L of thiocyanate was observed at a pH of 9.5. As with the results from jar tests with varying coagulant addition, the results from jar tests with varying pH show similar results in maximum removals for alum and ferric chloride. This is attributed to approximately equal volumes of floc.

Conclusions

The following conclusions can be drawn based on the results of experiments conducted during the project.

Carbon Adsorption

Data from batch carbon adsorption experiments were fitted quite well with the Freundlich isotherm. These isotherms revealed that the ranking of the four compounds from lowest to highest affinity for activated carbon was: thiocyanate, acetone, propionitrile, and pyrrole. Relative quantities of each compound adsorbed from multiple solute solutions revealed the same ranking by mole fractions. Specifically, the mole fractions for the adsorption of acetone, propionitrile, pyrrole, and thiocyanate from multiple solute solutions were 0.17, 0.23, 0.49, and 0.11, respectively. This order of affinity was reasonable based on the properties of the compounds, but adsorption was more directly related to the solubility of each compound.

Pyrrole has the highest molecular weight, the lowest solubility, and the lowest degree of polarity, thus it has the highest affinity for activated carbon. Propionitrile is more polar than acetone and has a lower molecular weight, but its lower solubility, apparently the most important factor, gives it a higher affinity for activated carbon.

Acetone and thiocyanate have identical molecular weights and both are very soluble, but thiocyanate has the lower affinity for activated carbon. The ionic character of the thiocyanate was undoubtedly a major cause of the different results in adsorption for the two compounds.

The adsorbances of all four of the compounds were low in comparison to compounds such as bis (2-ethylhexyl) phthalate for which thousands of milligrams can be removed per gram of carbon at a final concentration of only 1 mg/L. Adjustments to pH of the wastewater solution did not significantly affect adsorption of the compounds. All four compounds have relatively low affinities for activated carbon and that experimental conditions did not adversely affect the adsorption process.

A significant decrease in adsorption from multiple solute solutions was not seen for any of the compounds as would be expected for compounds that are very highly adsorbed onto activated carbon. A slight interference in the adsorptions of pyrrole and propionitrile from multiple solute solutions was seen because of their higher affinities for activated carbon. No interference was seen for the adsorption of acetone from multiple solute experiments. A slight interference was observed in the adsorption of thiocyanate from multiple solute solutions. This is believed to be related to the slower rate of adsorption of thiocyanate as well as its ionic character. No additional interference was seen in the adsorption of the compounds from spiked biological effluent. Even pyrrole, the most highly adsorbed compound, did not demonstrate an interference in adsorption onto activated carbon from a multiple solute solution containing an additional 40 mg/L of COD.

It is concluded that an activated carbon process could be used to remove acetone, propionitrile, pyrrole, and thiocyanate from a wastewater; however, relatively large quantities of carbon would be needed because of the relatively low affinities of the compounds for activated carbon. It is also concluded that the activated carbon process could be used as a polishing process to follow biological treatment of the compounds. The results indicate that low concentrations of acetone, propionitrile, pyrrole, and thiocyanate would be readily removed from solution. The biological endproducts would also

unrelated to pH. Removals of the four compounds at all pH values were low with removals of acetone, propionitrile, and pyrrole being about 20 mg/L and removals of thiocyanate ranging from 10 to 17 mg/L. If one pH value was to be selected as superior, it would be a pH of 9 where removals of all four compounds were slightly greater than at the other pH values.

Alum

The results from jar tests conducted at a pH of 7 with alum additions ranging from 0 to 600 mg/L are shown in Figure 6-63. Removals of the acetone, propionitrile, and pyrrole were proportional to alum addition up to 500 mg/L, while removals of thiocyanate did not increase at alum concentrations greater than 100 mg/L. At a concentration of 500 mg/L, removals of about 15 mg/L were observed for acetone, propionitrile, and pyrrole while removals of about 30 mg/L were observed for thiocyanate at concentrations of 100 mg/L and greater.

The volume of floc formed at an alum addition of 500 mg/L was about 100 ml following sedimentation. No observable change in the volume of floc was seen at an alum addition of 600 mg/L. It is concluded that the removals of acetone, propionitrile, and pyrrole were a result of adsorption onto the floc, because when the volume of floc increased with increasing alum addition up to 500 mg/L, the removals of these three compounds also increased. It is also concluded, however, that the removal of thiocyanate by alum may have been by a mechanism other than adsorption onto the floc because removals did not increase at alum additions greater than 100 mg/L even though floc volumes did. It is also interesting to note that the removals of acetone, propionitrile, and pyrrole with 100 mg/L of ferric chloride were very similar to their removals with 500 mg/L of alum. These two coagulant additions yielded similar volumes of floc, and thus similar reductions in concentrations of acetone, propionitrile, and pyrrole, further indicating removals of these compounds by adsorption onto the floc.

Figure 6-64 shows the results from jar tests conducted to determine the removals of the four compounds as a function of pH. The alum concentration used was 500 mg/L, and the initial concentrations of acetone, propionitrile, pyrrole, and thiocyanate were 97.2, 96.4, 96.7, and 99.5 mg/L, respectively. The results (Figure 6-64) show that the removals of the compounds were greatest at a neutral pH, while decreased removals were observed at higher and lower pH values. Maximum removals of about 23 mg/L were observed at a pH of 6.5 for acetone, propionitrile, and pyrrole, while a maximum removal of 32 mg/L of thiocyanate was observed at a pH of 9.5. As with the results from jar tests with varying coagulant addition, the results from jar tests with varying pH show similar results in maximum removals for alum and ferric chloride. This is attributed to approximately equal volumes of floc.

Conclusions

The following conclusions can be drawn based on the results of experiments conducted during the project.

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be successfully removed as indicated by consistent removals of the COD by activated carbon. Thus, activated carbon appears to be a useful process in the treatment of wastewaters containing acetone, propionitrile, pyrrole, and thiocyanate.

Chemical Coagulation/Precipitation

The results from the jar tests indicate that chemical coagulation/precipitation of the four compounds was unsuccessful. Removals of the compounds increased with increasing quantities of floc in the experiments with ferric chloride indicating that adsorption onto the floc was the mechanism by which the compounds were removed; however, the removals were very low. Maximum removals of acetone, propionitrile, and pyrrole were about 20% at a ferric chloride addition of 100 mg/L while the maximum removal of thiocyanate was 17%.

In experiments with alum, adsorption onto the floc appeared to be the mechanism for removal of acetone, propionitrile, and pyrrole. Again very low removals were seen with a maximum of 15% of acetone, propionitrile, and pyrrole being removed at an alum addition of 500 mg/L. A maximum of 32% of thiocyanate was removed at alum additions of 100 mg/L and greater. Since the removal of thiocyanate did not increase as the quantity of floc increased with alum additions greater than 100 mg/L, it was concluded that a mechanism other than adsorption onto the floc was responsible for the decrease in thiocyanate concentration.

It is concluded that chemical coagulation/precipitation is not a useful process for the removal of acetone, propionitrile, pyrrole, and thiocyanate from wastewaters.

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Subtask 6.3. Heavy Metals Removal

Introduction

The Eastern oil shale resource could be used to produce fuels to supplement current sources such as crude oil and natural gas and help alleviate future shortages. The retorting process extracts the oil from the shale, leaving behind the spent shale which must be disposed of safely. Although the spent shale currently meets EPA regulations regarding its disposal, these regulations are likely to become more stringent. In the event that the spent shale from the retorting process does not meet more stringent EPA regulations regarding the leaching of heavy metals from the shale, the spent shale must be pretreated to reduce the extent of heavy metal leaching. The kinetics of heavy metal dissolution are studied in order to select a treatment process that effectively reduces the levels of these heavy metals in the spent shale. This subtask was conducted by the University of Michigan (UM).

The first phase of the analysis is to determine the dissolution rates of selected heavy metals from shale in simple systems. The systems chosen were hydrochloric acid and nitric acid. The second phase is to develop methods of enhancing the dissolution rates of selected heavy metals using salts to catalyze the dissolution process. The results from the first phase are used as a benchmark in judging the effectiveness of the salt catalysis enhancement in the second phase. The information gained from these studies will aid in the development of processes required to reduce chromium, barium, and cadmium concentrations in spent shale below the limits considered environmentally acceptable for disposal.

Background

A typical analysis of Indiana (New Albany) oil shale reveals a large number of heavy metals present in trace quantities.¹ Because of limited time and resources, several heavy metals were selected for evaluation, including iron, barium, chromium and cadmium. Iron was chosen because it is relatively abundant in the oil shale (approximately 5% by weight) and because of its ease of analysis. Barium, chromium and cadmium were chosen because of their toxicity and potential as an environmental hazard. Table 6-29 contains a partial list of the trace element analysis of raw and hydrotreated Indiana (New Albany) shale (Appendix A gives a more complete listing).

Table 6-29. TRACE ELEMENTAL ANALYSIS OF INDIANA NEW ALBANY SHALE

Shale	<u>Raw</u>	<u>Retorted</u>
	-----	ppm -----
Element		
Barium	280	340
Cadmium	3.4	3.8
Chromium	62	70
Iron	45,000	51,000

be successfully removed as indicated by consistent removals of the COD by activated carbon. Thus, activated carbon appears to be a useful process in the treatment of wastewaters containing acetone, propionitrile, pyrrole, and thiocyanate.

Chemical Coagulation/Precipitation

The results from the jar tests indicate that chemical coagulation/precipitation of the four compounds was unsuccessful. Removals of the compounds increased with increasing quantities of floc in the experiments with ferric chloride indicating that adsorption onto the floc was the mechanism by which the compounds were removed; however, the removals were very low. Maximum removals of acetone, propionitrile, and pyrrole were about 20% at a ferric chloride addition of 100 mg/L while the maximum removal of thiocyanate was 17%.

In experiments with alum, adsorption onto the floc appeared to be the mechanism for removal of acetone, propionitrile, and pyrrole. Again very low removals were seen with a maximum of 15% of acetone, propionitrile, and pyrrole being removed at an alum addition of 500 mg/L. A maximum of 32% of thiocyanate was removed at alum additions of 100 mg/L and greater. Since the removal of thiocyanate did not increase as the quantity of floc increased with alum additions greater than 100 mg/L, it was concluded that a mechanism other than adsorption onto the floc was responsible for the decrease in thiocyanate concentration.

It is concluded that chemical coagulation/precipitation is not a useful process for the removal of acetone, propionitrile, pyrrole, and thiocyanate from wastewaters.

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$$-r'_A = k C_A^n \quad (6-16)$$

The reactant in this case is the particular acid being considered (hydrochloric acid or nitric acid). The specific rate constant, k , and reaction order, n , are parameters to be determined experimentally using the method of initial rates. The parameters can be determined from the initial reactant concentration, C_{A0} , and the initial dissolution rate, $-r'_{A0}$, by linearization of Equation 6-16, as shown in Equation 6-17.

$$\log(-r'_{A0}) = \log(k) + n \log(C_{A0}) \quad (6-17)$$

If the initial rate of reaction can be determined and the initial acid concentration is known, then a simple log-log plot of rate versus initial acid concentration will produce a straight line with slope n and intercept $\log(k)$, assuming that the power law model adequately describes the kinetics of the system.

In addition to the power law form of the rate equation, the Langmuir-Hinshelwood approach is often used to develop a mechanism for heterogeneous reactions. The rate law takes the form of Equation 6-18. The specific rate constant, k , and the equilibrium constant, K , are determined from initial rate data using the linearized form of Equation 6-18, as shown in Equation 6-19.

$$r = \frac{k C_A}{1 + K C_A} \quad (6-18)$$

$$\frac{1}{r} = \frac{K}{k} + \frac{1}{k C_A} \quad (6-19)$$

In these rate laws, the acid concentration was used as the parameter that determined the reaction rate. A more rigorous approach requires that the reactant activity be used in the rate law expressions. However, activities are often difficult to measure or estimate accurately. Thermodynamics provides a compromise since at low concentrations, the activity is proportional to the concentration. In some sections of this report, rate laws are presented based on both concentration, C_A , and activity, a_A .

The determination of the initial rate is made by analysis of concentration versus time data. During the initial stage of reaction, the change in the reactant concentration is insufficient to alter the reaction rate. As a result, the concentration of the heavy metal in solution, C_B , initially rises linearly with time. The slope of this line, as determined by a least squares procedure, is then the initial rate of dissolution. It is often the case where the reaction proceeds rapidly such that not enough samples can be taken during the initial rates period to determine a slope by a simple least squares analysis. In this case, an interpolating function is fit to the data and the slope at $t = 0$ is obtained analytically from the interpolating function. The interpolating function used was:

$$C_B(t) = a + b(1 - e^{-ct}) \quad (6-20)$$

The goal of the initial phase of this study was to describe the kinetics of the dissolution of heavy metals from oil shale in simple systems consisting only of aqueous mineral acids. A description of the rates of dissolution in acidic media is required in order to judge the effectiveness of methods applied to enhance the heavy metal dissolution rates.

The second phase of the study is to determine a method of enhancing the dissolution rates and to evaluate the effectiveness of the method using the dissolution rates obtained in aqueous acidic systems as a benchmark. The addition of salts to acidic media is known to affect the dissolution rates of materials.²⁻¹⁰ Often the effect is due to an increase in the activity of the reactive proton and the salt does not actually participate in the dissolution process beyond its effect on the activity. Sometimes this effect is due to a participation of the salt in the mechanism of the dissolution process. The work of Kline and Fogler² has shown that the addition of salts to hydrofluoric acid systems can catalyze the dissolution of aluminosilicate minerals. Therefore, salt catalysis was the method chosen to enhance the dissolution rates of the selected heavy metals from oil shale. The salts chosen include sodium chloride, sodium nitrate, and ammonium nitrate.

The large number of heavy metals present in shale and the possibility of the heavy metals being incorporated in various forms (for example, oxides, sulfides, etc.) makes it virtually impossible to estimate kinetic parameters for individual reactions. Furthermore, a detailed analysis of compounds in Indiana New Albany shale is not available.

Model compounds are often employed to simplify complex systems, allowing specific information to be determined. This determination is made with the expectation that the results can be applied to the original complex system. The model compound approach was applied to heavy metal dissolution from shale to remove the complication caused by the presence of such a large number of heavy metals. Cadmium sulfide was selected as the model compound because cadmium is one of the metals selected for study.

Kinetic Rate Laws

The study of the dissolution kinetics of heavy metals from shale is complicated by several of the properties of shale. First, the composition and physical properties of the raw shale vary from one type of shale to the next. Second, the shale is composed of many different chemical species. A particular heavy metal species can be represented in the shale in a variety of different forms, for example, oxides, sulfates, etc. The study of the dissolution of each of these compounds for each metal in shale is not practical in the scope of this subtask. Therefore, no attempt was made to try to determine the kinetics of the dissolution of each form of the selected heavy metals. Instead, the bulk removal rate of each heavy metal species was studied. Evaluation of several shales was beyond the scope of work in this study, therefore, Indiana New Albany shale was used for all experiments.

The power law form of the kinetic rate expression is often used to describe the dissolution behavior of elementary reaction systems and systems not well characterized. This model was used to describe, quantitatively, the acidic dissolution of the selected heavy metals from oil shale. The power law model presumes that the dissolution rate is proportional to the reactant concentration to some power.

Figure 6-65. SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS USED IN THE SHALE SLURRY EXPERIMENTS (The Samples Drawn by Pipet are Filtered Through $0.45\ \mu\text{m}$ Filter Paper)

Results and Discussion

Dissolution in Acids

Retorted Shale

The raw data obtained for iron, barium, cadmium and chromium dissolution from hydroretorted Indiana New Albany shale are presented in Figures 6-66 to 6-73. Where there was distinct curvature in the data, an interpolating function was applied and the initial rate was estimated from the derivative of the function at the origin. Figures 6-74 and 6-75 show the correlation of the logarithm of the initial rate to the logarithm of the initial acid concentration and Table 6-30 lists the kinetic parameters describing the power law expression based on acid concentration.

Over the concentration ranges studied, the logarithm of the initial rate is approximately linearly related to the logarithm of the initial acid concentration. This indicates that the power law kinetic rate expression provides a reasonable description of the dissolution rate as a function of acid concentration in the range of acid concentrations studied. Rajeshwar *et al.*¹² whose work concentrated on metal ions abundant in shale including iron, reported that ion yields for Green River oil shale were independent of hydrogen and chloride ion concentrations over the range of 3.3 N to 11 N hydrochloric acid. Research at the University of Michigan has shown that this

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The power law form of the kinetic rate expression is often used to describe the dissolution behavior of elementary reaction systems and systems not well characterized. This model was used to describe, quantitatively, the acidic dissolution of the selected heavy metals from oil shale. The power law model presumes that the dissolution rate is proportional to the reactant concentration to some power.

Figure 6-68. CONCENTRATIONS MEASURED FOR IRON DISSOLUTION FROM RETORTED SHALE USING HYDROCHLORIC ACID

Figure 6-69. CONCENTRATIONS MEASURED FOR IRON DISSOLUTION FROM RETORTED SHALE USING NITRIC ACID

Figure 6-66. CONCENTRATIONS MEASURED FOR BARIUM DISSOLUTION FROM RETORTED SHALE USING HYDROCHLORIC ACID

Figure 6-67. CONCENTRATIONS MEASURED FOR BARIUM DISSOLUTION FROM RETORTED SHALE USING NITRIC ACID

Figure 6-72. EFFECT OF LOW NITRIC ACID CONCENTRATION ON CHROMIUM DISSOLUTION

Figure 6-73. EFFECT OF HIGH NITRIC ACID CONCENTRATION ON CHROMIUM DISSOLUTION

Figure 6-66. CONCENTRATIONS MEASURED FOR BARIUM DISSOLUTION FROM RETORTED SHALE USING HYDROCHLORIC ACID

Figure 6-67. CONCENTRATIONS MEASURED FOR BARIUM DISSOLUTION FROM RETORTED SHALE USING NITRIC ACID

Table 6-30. POWER LAW PARAMETERS (Based on Concentration) DETERMINED FROM INITIAL RATES DATA FOR THE DISSOLUTION OF SELECTED HEAVY METALS FROM RETORTED INDIANA NEW ALBANY SHALE

<u>Element</u>	<u>Acid</u>	<u>k</u>	<u>n</u>
Fe	HCl	1.0×10^{-6}	0.43
	HNO ₃	6.9×10^{-7}	0.32
Ba	HCl	1.8×10^{-9}	0.58
	HNO ₃	1.8×10^{-9}	0.74
Cd	HCl	6.9×10^{-10}	0.14
	HNO ₃	5.1×10^{-10}	0.80
Cr	HCl	6.2×10^{-10}	1.35
	HNO ₃	3.8×10^{-10}	0.75

is not the case for iron at lower hydrogen ion concentrations nor is it true for the other elements selected for study.

The power law form of the rate law was also evaluated using activities instead of concentrations (Figures 6-76 and 6-77). As expected, the models differ only in the specific rate constant, k. Due to the similarity in the initial rates determined for iron and barium dissolution in hydrochloric acid and nitric acid, especially when compared in terms of acid activity, it was decided to treat the dissolution as independent of the anion and estimate the kinetic parameters using the combined set of data. These parameters, along with those determined for the rest of the selected heavy metals, are given in Table 6-31. As Figure 6-77 shows, chromium and cadmium dissolution from retorted shale are clearly dependent on the differences between hydrochloric acid and nitric acid.

The initial rate data were also analyzed to determine if the Langmuir-Hinshelwood rate law could be applied to the dissolution of iron, barium, cadmium or chromium. As Figures 6-78 and 6-79 show, plotting the reciprocal initial rate versus the reciprocal acid concentration produced straight lines for the dissolution of cadmium and chromium from retorted shale. The results for iron and barium dissolution produced plots with definite curvature indicating that the Langmuir-Hinshelwood approach does not apply under these conditions. The kinetic parameters determined are presented in Table 6-32. Notice however that the equilibrium constant, K, for chromium dissolution in hydrochloric acid is negative, which is not possible for the Langmuir-Hinshelwood model. A closer look at the initial rates determined for chromium dissolution by both hydrochloric and nitric acid shows a definite inflection suggesting that a rate law of a different form will better describe the dissolution process.

Figure 6-74. INITIAL RATES FOR IRON AND CADMIUM DISSOLUTION FROM RETORTED SHALE

Figure 6-75. INITIAL RATES FOR BARIUM AND CHROMIUM DISSOLUTION FROM RETORTED SHALE

Table 6-31. POWER LAW PARAMETERS (Based on Acid Activity) DETERMINED FROM INITIAL RATES DATA FOR THE DISSOLUTION OF SELECTED HEAVY METALS FROM RETORTED INDIANA NEW ALBANY SHALE

Element	Acid	k	n
Fe	HCl	1.4×10^{-6}	0.62
	HNO ₃	7.7×10^{-7}	0.33
	Acid	9.6×10^{-7}	0.43
Ba	HCl	2.5×10^{-9}	0.69
	HNO ₃	2.3×10^{-9}	0.78
	Acid	2.4×10^{-9}	0.75
Cd	HCl	7.0×10^{-10}	0.17
	HNO ₃	6.8×10^{-10}	0.82
Cr	HCl	6.9×10^{-10}	1.26
	HNO ₃	4.5×10^{-10}	0.71

Figure 6-78. APPLICATION OF LANGMUIR-HINSHELWOOD KINETICS TO THE INITIAL RATES FOR CHROMIUM DISSOLUTION FROM RETORTED SHALE IN HYDROCHLORIC AND NITRIC ACIDS

Figure 6-74. INITIAL RATES FOR IRON AND CADMIUM DISSOLUTION FROM RETORTED SHALE

Figure 6-75. INITIAL RATES FOR BARIUM AND CHROMIUM DISSOLUTION FROM RETORTED SHALE

The results obtained can be applied directly to determining the ability of the acid to dissolve one heavy metal while leaving another in the shale. Such a selective dissolution would be desirable in order to minimize waste treatment costs. The selectivity, defined as the ratio of the dissolution rates for the two heavy metals, is given by --

$$S_{A/B} = \frac{r_A}{r_B} = \frac{k_A}{k_B} a_{\text{acid}}^{(n_A - n_B)} \quad (6-21)$$

For example, the specific selectivity (for example, unit acid activity) of hydrochloric acid to iron and barium is --

$$S_{\text{Fe/Ba}} = \frac{r_{\text{Fe}}}{r_{\text{Ba}}} = \frac{9.6 \times 10^{-7}}{2.4 \times 10^{-9}} = 4.0 \times 10^2$$

The concept of selectivity can also be applied to the dissolution of a specific element by two different acids, or, more generally, two different systems. Equation 6-21 requires only slight modification for this added generality, namely that the acid activity for one system is not the same as the acid activity for the second. This definition of selectivity refers to the capacity of one system to remove a particular species relative to the capacity of a second system to remove the same species from shale.

$$S_{A/B} = \frac{r_A}{r_B} = \frac{k_A a_A^{n_A}}{k_B a_B^{n_B}} \quad (6-22)$$

For example, the dissolution of chromium from hydroretorted shale is more sensitive to acid activity when using hydrochloric acid than when using nitric acid. This is evident from the reaction orders, 1.26 for dissolution in hydrochloric acid and 0.71 for dissolution in nitric acid. Note also that since the reaction order is not the same for both acids, there will be a range of acid activities for which nitric acid will give a better selectivity than hydrochloric. There will also be a range where the reverse is true.

Raw Shale

The results of the dissolution of iron and barium from raw shale indicated that the dissolution process was different than the process in retorted shale. The metal ion concentrations rose quickly and then decreased. Figures 6-80 and 6-81 show some typical results for barium and iron dissolution obtained using raw shale. In both cases an initial rise and fall in iron and barium concentration was observed.

One possible mechanism for the behavior observed for iron dissolution from raw shale in 0.01 M hydrochloric acid involves the precipitation of iron(II) hydroxide and iron(III) hydroxide as the solution pH rises. As the reaction proceeds, heavy metals are removed from shale by acidic dissolution. The process depletes the hydrogen ion concentration and the pH rises. The solubility product constants of iron(II) hydroxide and iron(III) hydroxide are

Figure 6-79. APPLICATION OF LANGMUIR-HINSHELWOOD KINETICS TO THE INITIAL RATES FOR CADMIUM DISSOLUTION FROM RETORTED SHALE IN HYDROCHLORIC AND NITRIC ACIDS

Table 6-32. KINETIC PARAMETERS FOR LANGMUIR-HINSHELWOOD RATE LAW AS APPLIED TO HEAVY METAL DISSOLUTION FROM RETORTED INDIANA NEW ALBANY SHALE

<u>Metal</u>	<u>Acid</u>	$K \frac{\text{dm}^3}{\text{gmol}}$	$k \frac{\text{dm}^3}{\text{gm} - \text{min}}$
Cd	HCl	117	7.46×10^{-8}
Cd	HNO ₃	0.735	8.90×10^{-10}
Cr	HCl	-30.4	3.16×10^{-10}
Cr	HNO ₃	1.07	7.75×10^{-10}

4.87×10^{-17} and 2.64×10^{-39} , respectively.¹³ Consequently, as the pH rises, these iron compounds begin to precipitate. Water dissociation replenishes the hydrogen and hydroxide ion concentrations in response to the removal of hydrogen by acidic dissolution of heavy metals and the removal of hydroxide by the precipitation of iron hydroxides. Eventually a steady state is reached and the precipitation rate matches the dissolution rate. Only the iron dissolved in the liquid phase is detected by atomic absorption because the precipitate is retained on the filter paper with the raw shale. The iron concentration can, therefore, reach a maximum and the rate decays to zero as the steady state is approached.

The precipitation of iron was not observed in the retorted shale because the hydrogen ion concentration did not increase as drastically as it did for the raw shale. Figure 6-82 shows the pH as a function of time for two experiments conducted in 0.01 M hydrochloric acid with raw and retorted shale. The pH in the raw shale experiment went from 2.0 to about 7.5 in 90 minutes. The pH in the retorted shale experiment changed from 2.0 to 2.4 in the same amount of time. These measurements show that the hydrochloric acid was exhausted in the shale slurry.

Figure 6-82. pH MEASURED DURING COURSE OF EXPERIMENT WITH AN INITIAL HYDROCHLORIC ACID CONCENTRATION OF 0.01 MOLAR

A substantial amount of the iron in Kentucky New Albany shale is distributed as Fe(II) ,¹⁴ and it is reasonable to assume that the same is true of Indiana New Albany shale. Based on the iron concentration and the pH measured, the hydroxide concentration rose to the level needed to precipitate

Figure 6-79. APPLICATION OF LANGMUIR-HINSHELWOOD KINETICS TO THE INITIAL RATES FOR CADMIUM DISSOLUTION FROM RETORTED SHALE IN HYDROCHLORIC AND NITRIC ACIDS

Table 6-32. KINETIC PARAMETERS FOR LANGMUIR-HINSHELWOOD RATE LAW AS APPLIED TO HEAVY METAL DISSOLUTION FROM RETORTED INDIANA NEW ALBANY SHALE

<u>Metal</u>	<u>Acid</u>	<u>K</u> $\frac{\text{dm}^3}{\text{gmol}}$	<u>k</u> $\frac{\text{dm}^3}{\text{gm} - \text{min}}$
Cd	HCl	117	7.46×10^{-8}
Cd	HNO ₃	0.735	8.90×10^{-10}
Cr	HCl	-30.4	3.16×10^{-10}
Cr	HNO ₃	1.07	7.75×10^{-10}

Table 6-33. RELATIVE DISSOLUTION RATES* FOR ACID-SALT SYSTEMS
STUDIED SHOWING THE ENHANCEMENT OBTAINED BY SALT CATALYSIS

<u>0.1 M Nitric Acid/Sodium Nitrate</u>			
<u>Salt</u>	<u>Iron</u>	<u>Barium</u>	<u>Cadmium</u>
0.00	1.00	1.00	1.00
0.010	2.62	0.297	0.262
0.10	2.97	0.235	1.40
1.0			2.07

<u>0.1 M Hydrochloric Acid/Sodium Chloride</u>		
<u>Salt</u>	<u>Iron</u>	<u>Barium</u>
0.00	1.00	1.00
0.010	1.91	0.570
0.010	2.02	0.448
0.10	1.96	0.248

<u>1.5 M Nitric Acid/Ammonium Nitrate</u>	
<u>Salt</u>	<u>Chromium</u>
0.00	1.00
0.010	0.962
0.10	2.93
1.0	3.46

<u>0.1 M Hydrochloric Acid/Ammonium Nitrate</u>	
<u>Salt</u>	<u>Iron</u>
0.00	1.00
0.010	0.456
0.10	0.403
1.0	0.265
2.0	0.319

* The dissolution rate observed for the salt catalyzed systems are ratioed to the rate observed for the uncatalyzed systems.

iron(II) hydroxide, but not iron(III) hydroxide. The iron(II) begins to precipitate while the iron(III) continues to dissolve. This can account for the maximum observed in the iron dissolution experiment. The analysis of the mechanism cannot be carried further without a more detailed study of the kinetics of iron(II) and iron(III) dissolution, which is beyond the scope of this work.

Due to the complications encountered with the dissolution of heavy metals from raw shale, further study of the dissolution from raw shale was discontinued. The study of heavy metal removal under conditions that favor precipitation requires greater knowledge of the distribution of heavy metals on a compound basis because anion concentrations are needed to study the kinetics of precipitation. Anions are introduced into the system by the acidic solvent, by dissolution of the shale, and by decomposition of water and precipitated compounds. Such a study of raw shale was beyond the original scope of work, and retorted shale would be a more likely candidate for heavy metal removal prior to disposal than would raw shale.

Salt Catalysis of Heavy Metal Removal

The enhancement of the acidic dissolution rates of metal containing compounds by the addition of salt to the acidic media has been observed for a wide variety of situations.²⁻¹⁰ In some cases the effect is believed to be one of increased hydrogen ion activity. However, in many cases the effect is due to some other physical phenomenon. Kline and Fogler² report catalysis of the dissolution of aluminosilicates by the addition of acid and salt and attribute the acceleration of the dissolution rate to a mechanistic participation of the hydrogen ion and the salt cation. Similar findings were reported for the dissolution of galena in sodium chloride solutions⁶ and copper(II) sulfide in iron(III) chloride solutions.⁸ On the other hand, the dissolution of CuO in perchloric acid is enhanced through a change in the activity of the hydrogen ion by addition of sodium perchlorate.⁷ In more complicated cases, the accelerated rate is attributed to increases in the activity and a mechanistic participation of the salt.^{4,10}

The largest salt concentration possible was dictated not by the saturation limit of the salt in the acid, but instead by the performance of the atomic absorption unit. The large excess of salt in the samples interfered with the analysis. At salt concentration of about 2 molar or more, no useful information was obtained. This problem was even more pronounced with the chromium analysis of the nitric acid/sodium nitrate samples. Metal-containing nitrate salts (for example, calcium nitrate, lithium nitrate, and potassium nitrate) would produce unacceptable interference even at low concentrations. The interference was greatly reduced by using a non-metal salt where possible. Ammonium nitrate was chosen for this purpose.

Table 6-33 shows the dissolution rates of iron, barium, cadmium, and chromium from hydroretorted shale obtained by adding salts to the acid systems. In most cases the dissolution rate was increased by the addition of salt to the acid systems. However, in the case of barium dissolution using both nitric acid and hydrochloric acid, the relative rates (r/r_0 where r_0 is the rate in the corresponding uncatalyzed system) decreased to 0.2 when salt was added (sodium nitrate and sodium chloride) to 0.1 M acid (nitric acid and hydrochloric acid). Also, the relative dissolution rate of iron in 0.1 M

Figure 6-83. SCHEMATIC DIAGRAM OF THE APPARATUS USED IN THE CADMIUM SULFIDE MODEL COMPOUNDS EXPERIMENTS
(The Reaction Vessel is Constructed of Quartz Glass With an Optical Quality Window in the Bottom)

cadmium concentration in samples taken from the vessel represented the cadmium concentration in the bulk liquid phase. This was verified by comparing the last sample taken before removing the rotating disc to a sample taken after the disc was removed and the liquid stirred by hand.

Rotating the sample also reduced mass transfer resistances at the surface of the disc, guaranteeing that the system was operating in a reaction-rate limited regime. This was demonstrated by measuring the dissolution rate at various rotation rates (Figure 6-84). Levich¹⁶ showed that the dissolution rate for a rotating disc apparatus of the type used is proportional to $\sqrt{\omega}$, where ω is the rotation rate of the disc. It was determined that 800 RPM was sufficient to guarantee operation in the kinetically limited regime and to provide adequate stirring for the experiments conducted in halogenic acids and in hydrochloric acid-sodium chloride mixtures.

The procedure used in conducting the experiments was to immerse the disc in 100 to 200 mL of the solvent of interest and periodically withdraw a small sample of the liquid. The concentration of cadmium in the sample was then determined by atomic absorption (GBC 903 with graphite furnace attachment). An initial rate could be estimated by fitting a least-squares line to the concentration versus time data. The volume change of the system due to periodic sampling did not introduce a significant error into the results because the volume of the sample was small compared to the remaining volume in the vessel (typically less than 1%).

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Table 6-34. CADMIUM SULFIDE ACCUMULATION RATES IN DEIONIZED WATER AT VARIOUS ROTATION RATES

Rotation Rate, rpm	Accumulation Rate, g-mol/cm ² min
100	8.44×10^{-11}
300	8.66×10^{-10}
500	1.50×10^{-9}
600	1.64×10^{-9}
800*	2.00×10^{-9}

* Estimated by extrapolation.

Figure 6-85. CADMIUM SULFIDE ACCUMULATION RATES IN DEIONIZED WATER. RATE AT 800 rpm IS AN EXTRAPOLATION OF A CUBIC SPLINE FIT OF THE DATA

Figure 6-84. CADMIUM SULFIDE DISSOLUTION RATES AT VARIOUS ROTATION SPEEDS INDICATING OPERATION IN A KINETICALLY LIMITED REGIME

Results and Discussion

Deionized Water

The first set of experiments was conducted in deionized water in order to estimate the rate at which cadmium sulfide dislodges from the disc surface and becomes suspended in the liquid phase. Atomic absorption cannot distinguish from dissolved cadmium ions and suspended cadmium sulfide particulates since the solvent is first vaporized and the remaining sample atomized. The concentrations observed for the deionized water experiments were far in excess of the equilibrium cadmium concentration determined from the solubility product constant ($10^{-26.1}$ at 25°C).¹⁷ The accumulation rate at 800 rpm was approximated by a cubic spline extrapolation based on data taken at four rotation rates ranging from 100 to 600 rpm. Table 6-34 lists the rates observed and Figure 6-85 shows the rates correlated to $\sqrt{\omega}$.

Halogenic Acids

The next set of experiments were conducted with hydrochloric acid, hydrobromic acid and hydriodic acid from 0.01 M to about 1.0 M. The activity of the acids at the concentrations used were obtained from published results where available¹⁸ and estimated from Bromley's Model for strong electrolytes otherwise. Figure 6-86, a log-log plot of initial dissolution rate versus acid activity, shows the first order behavior of the rate with activity. Table 6-35 lists the specific reaction rates and reaction orders for the three acids and for the combined data set. The kinetic rate constants were not

Salt Catalysis

The salt catalysis of the acidic dissolution of cadmium sulfide was studied using sodium chloride additions to 1.0 M hydrochloric acid. The procedure followed was similar to that used in acidic dissolution studies. The rotating disc was placed in a 1.0 M hydrochloric acid solution and periodically sampled for about 8 minutes. At 8 minutes, an acidic salt solution was added to the reaction vessel and periodic sampling was continued. The acid concentration in the acidic salt solution was the same as that in the reaction vessel to prevent dilution of the acid. Dissolving the sodium chloride in a quantity of 1.0 M hydrochloric acid prior to addition to the reaction vessel was necessary to prevent the salt crystals from interacting with the disc surface and physically impacting, abrading and removing cadmium sulfide particles that would then dissolve in the bulk phase.

Figure 6-87 shows the results obtained for cadmium sulfide dissolution in 1.0 M hydrochloric acid with salt concentrations that range from 0.05 M to 1.5 M sodium chloride. The first half of each set of data (up to 8 minutes) represents the acid only case where no salt was present. The three rates for the dissolution in hydrochloric acid alone were determined by a least squares fit of a line to the data. The three rates averaged 9×10^{-8} g-mol Cd/cm²-min, which is consistent with the rate law developed for halogenic acids. The cadmium concentrations in the first 8 minutes for the three runs are represented in Figure 6-87 by a single straight line for clarity. At 8 minutes, a solution of 1 M hydrochloric acid and twice the desired final concentration of sodium chloride was added to the reaction vessel and sampling was continued. The dissolution rate during this time was also determined by a least squares fit of a straight line to the data.

Figure 6-87. RAW DATA FOR CADMIUM SULFIDE MODEL COMPOUND DISSOLUTION IN 1.0 M HYDROCHLORIC ACID WITH SODIUM CHLORIDE

Figure 6-84. CADMIUM SULFIDE DISSOLUTION RATES AT VARIOUS ROTATION SPEEDS INDICATING OPERATION IN A KINETICALLY LIMITED REGIME

Results and Discussion

Deionized Water

The first set of experiments was conducted in deionized water in order to estimate the rate at which cadmium sulfide dislodges from the disc surface and becomes suspended in the liquid phase. Atomic absorption cannot distinguish from dissolved cadmium ions and suspended cadmium sulfide particulates since the solvent is first vaporized and the remaining sample atomized. The concentrations observed for the deionized water experiments were far in excess of the equilibrium cadmium concentration determined from the solubility product constant ($10^{-26.1}$ at 25°C).¹⁷ The accumulation rate at 800 rpm was approximated by a cubic spline extrapolation based on data taken at four rotation rates ranging from 100 to 600 rpm. Table 6-34 lists the rates observed and Figure 6-85 shows the rates correlated to $\sqrt{\omega}$.

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same degree. Furthermore, iron dissolution rates could be enhanced by the addition of sodium nitrate but retarded by the addition of ammonium nitrate. This means that salt additions can enhance or retard heavy metal dissolution, but care must be taken in choosing the right acid salt combination based on how much enhancement is desired and what elements are to be removed.

The work with the model compound showed that cadmium sulfide dissolution in halogenic acids obeys first order kinetics with respect to acid concentration. The work also showed that the dissolution rate is affected by the presence of salt in a manner similar to heavy metal dissolution (including cadmium) from retorted shale. Enhancements of a factor of approximately 300% were commonly observed. The results also showed that a simple correlation between the parameters for the dissolution of the cadmium sulfide model compound and the cadmium dissolution from oil shale is not possible. The rate laws for cadmium dissolution from retorted shale showed a reaction order of 0.14 with respect to acid concentration. This indicates that cadmium is present in retorted shale in more forms than just cadmium sulfide.

Future Work

Due to the large number of constituent heavy metals and the variety of heavy metal compounds present in oil shale, further study of heavy metal removal should be limited to studying the kinetic properties of the bulk metal ions. A more comprehensive chemical analysis of the constituent compounds will be required for a fundamental approach to the kinetics of heavy metal removal. Model compounds can be used to determine kinetic parameters, but without knowing how the compounds are distributed there is little hope of modeling the system from first principles.

The studies of this research were conducted in a kinetically limited regime. This required grinding of the shale and keeping the system well mixed. Both of these processes are energy intensive and may not be necessary. Once the bulk kinetics of heavy metal removal have been determined, the next step is to discover at what point the metals are being removed most effectively and this does not necessarily entail that the highest kinetic rates should be maintained. It is, therefore, recommended that the effects of particle size and mixing on heavy metal removal rates be investigated.

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The results show an increase in dissolution rate with increasing salt concentration. Adjusting the hydrogen ion activity for sodium chloride concentration (using Bromley's Method to estimate activities) could not explain the observed rate increases, thus indicating that the enhancement is due to the participation of the salt species in the dissolution mechanism. The results obtained for the dissolution of cadmium sulfide in halogenic acids without additional salts showed that there was no difference between the acids, implying that the anion contributed by the acid did not affect the dissolution rate. The participation of the sodium cation is, therefore, the more likely cause of the rate enhancement. Table 6-36 lists the rates and relative rates determined from the salt catalysis data.

Table 6-36. INITIAL RATES DETERMINED FOR SODIUM CHLORIDE CATALYSIS OF THE DISSOLUTION OF CADMIUM SULFIDE IN 1.0 MOLAR HYDROCHLORIC ACID

$C_{\text{NaCl}},$ g-mol/dm ³	Rate, g-mol Cd/cm ² min	Relative Rate
0.00	8.77×10^{-8}	1.00
0.050	1.28×10^{-7}	1.46
0.50	2.12×10^{-7}	2.41
1.5	3.40×10^{-7}	3.87

The question remains as to whether the cation participates with the hydrogen ion or rather simply in addition to the hydrogen ion. Experiments run in 0.01 M and 0.1 M aqueous sodium chloride produced dissolution rates commensurate with rates observed in distilled water only. The rate observed for 1.0 M aqueous sodium chloride was about 10% of the specific rate for cadmium sulfide dissolution in halogenic acids. These results indicate that the salt is behaving as a catalyst and has no dissolution capacity without the presence of the hydrogen ion.

Conclusions

The results from the studies of heavy metal removal using only nitric acid or hydrochloric acid showed that the dissolution of iron, barium, cadmium, and chromium from retorted Indiana New Albany shale can be described approximately by a power law model over a range of concentrations from 0.1 molar acid to 1.0 molar acid. Using acid activity in place of acid concentrations in the rate law indicates that there is little difference between hydrochloric acid and nitric acid with respect to the dissolution rate of iron and barium. This was not the case for cadmium and chromium dissolution, indicating that the mechanism is not based solely on the proton concentration.

The use of salts has been shown to be an effective means of enhancing or retarding the dissolution of heavy metals from oil shale. Typical enhancements observed for some systems were about 2 to 3 times the rates observed for systems without salt, indicating that the salt does indeed behave as a catalyst. The same systems retarded dissolution rates of barium by about the

Subtask 6.4.1. PFH System Analyses

Objective

The objective of this subtask was to define the effluent streams, quantities and compositions for a pressurized fluidized-bed hydroretorting (PFH) plant utilizing various Eastern raw and beneficiated oil shales. A computer program was to be developed to provide a detailed analysis including --

- Simulation of the PFH Process based on data obtained in other program tasks
- Material balances of the major stream constituents and energy balance in the system
- Potential pollutants contained in the process streams
- Evaluation of capacity and economics for a commercial PFH plant.

Background

The existing computer program that simulates a moving-bed hydroretorting plant based on the HYTORT process is the cornerstone for development of the computer program for the PFH process. The program is based on a conceptual commercial moving-bed hydroretorting plant shown in Figure 6-88. The plant includes the following major process areas:

- Hydroretort
- Product Gas/Oil Phase Separation
- Light Oil Separation
- Ammonia Removal
- Ammonia Recovery
- Sulfur Removal
- Sulfur Recovery
- Hydrogen Recovery
- Hydrogen Production
- Water Treatment
- Miscellaneous Heater, Condensers, Compressors, etc.

The program is modular in organization and consists of the main program and 61 subroutines for calculating thermophysical properties such as enthalpy and dew point, and different unit operations such as gas cooling, gas scrubbing, oil flashing, retorting, quenching, etc. Material balances are

The results show an increase in dissolution rate with increasing salt concentration. Adjusting the hydrogen ion activity for sodium chloride concentration (using Bromley's Method to estimate activities) could not explain the observed rate increases, thus indicating that the enhancement is due to the participation of the salt species in the dissolution mechanism. The results obtained for the dissolution of cadmium sulfide in halogenic acids without additional salts showed that there was no difference between the acids, implying that the anion contributed by the acid did not affect the dissolution rate. The participation of the sodium cation is, therefore, the more likely cause of the rate enhancement. Table 6-36 lists the rates and relative rates determined from the salt catalysis data.

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The question remains as to whether the cation participates with the hydrogen ion or rather simply in addition to the hydrogen ion. Experiments run in 0.01 M and 0.1 M aqueous sodium chloride produced dissolution rates commensurate with rates observed in distilled water only. The rate observed for 1.0 M aqueous sodium chloride was about 10% of the specific rate for cadmium sulfide dissolution in halogenic acids. These results indicate that the salt is behaving as a catalyst and has no dissolution capacity without the presence of the hydrogen ion.

Conclusions

The results from the studies of heavy metal removal using only nitric acid or hydrochloric acid showed that the dissolution of iron, barium, cadmium, and chromium from retorted Indiana New Albany shale can be described approximately by a power law model over a range of concentrations from 0.1 molar acid to 1.0 molar acid. Using acid activity in place of acid concentrations in the rate law indicates that there is little difference between hydrochloric acid and nitric acid with respect to the dissolution rate of iron and barium. This was not the case for cadmium and chromium dissolution, indicating that the mechanism is not based solely on the proton concentration.

The use of salts has been shown to be an effective means of enhancing or retarding the dissolution of heavy metals from oil shale. Typical enhancements observed for some systems were about 2 to 3 times the rates observed for systems without salt, indicating that the salt does indeed behave as a catalyst. The same systems retarded dissolution rates of barium by about the

calculated by trial and error utilizing the Newton-Raphson method to achieve convergence. The program provides material and energy balances for the given input if closure is possible based on different assumptions. The program structure is shown in Figure 6-89.

A model to simulate the PFH process as the heart of the plant is shown in Figure 6-90. This model is described briefly below.

- The entire bed is divided into three independent zones: preheat zone, retort zone, and cooling zone based on the shale temperatures assigned.
- The product gas/oil (Stream 4) drawn off above the retort zone does not mix with the secondary recycle gas (Stream 5) added between the retort zone and the preheat zone.
- The products in all chemical processes are fixed and given as inputs.
- The temperature approach for heat transfer between the solid stream and gas flow is 10°F (5.5°C).
- In the preheat zone:
 - The exit shale temperature is assigned
 - All shale moisture and 20% of the water produced in the process is vaporized and evolved
 - 50% of the H₂S produced is evolved
 - The temperature of the gas exiting the preheat zone is required to be 25°F (13.9°C) above the condensation temperature of the gas.
- In the retort zone:
 - The exit shale temperature is assigned
 - The composition of the product gas/oil are given as inputs
 - The temperature of the first recycle gas (Stream 2) is assumed
- In the cooling zone:
 - No chemical reaction occurs
 - The composition and temperature of the feed gas are assumed and finally determined from downstream system analysis.

The input for the moving-bed hydroretorting program has typically been derived from mini-batch (MBU) or bench-scale (BSU) unit data obtained from IGT. The data is prepared for input into the program by the following procedure --

1. The material balance is closed via specific rules

PFH.DRW, 9/80

Figure 6-88. SCHEMATIC FLOW DIAGRAM OF MOVING BED HYDRORETORTING PLANT

Figure 6-90. MODEL OF THE PFH RETORT

PFH.DRW, 9/90

Figure 6-88. SCHEMATIC FLOW DIAGRAM OF MOVING BED HYDRORETORTING PLANT

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RUN: PFH05-88

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2. The oil yield is adjusted for particle size differences
3. The flows are scaled up to an appropriate commercial design basis (that is, 50,000 bbl/day or other).

The program can provide numerical results in terms of gas/oil production, pollutant emissions, and evaluations of both capital and operating costs according to various input data such as plant size, shale properties, and reaction parameters. However, in simulating the commercial operation, rigorous thermodynamic equilibrium calculations for the reaction, flash, and phase change, are not performed. The reaction parameters, production rate and the simple fixed split factors are given as input data based on an earlier conceptual plant design by Bechtel Group, Inc., and some experimental results. Therefore, such empiric or designed parameters could not be changed significantly for the purpose of parametric studies.

The program was run using a set of data from a test (MBU-5) conducted at IGT in the MBU with Indiana New Albany shale. The program ran successfully for different input parameters such as hydrogen purity and reaction conditions. The results show that the assumed reaction conditions have a significant affect on the products. The criteria for convergence was also found to be sensitive to the initial hydrogen purity guess, because a small tolerance is required for the 16 components of the gas mixture. An example of typical output from the computer program is shown in Figure 6-91.

A printout of the FORTRAN code for the moving-bed hydroretorting program was obtained by IGT from HYCRUDE Corporation. The portion of the program that required significant modification was the section that simulates the moving-bed HYTORT reactor. This section required rewriting to simulate a PFH reactor.

Computer Simulation of PFH Process

The existing computer program for a moving-bed hydroretorting plant was modified to simulate a PFH plant.

As a first step of the system analysis, the existing program was separated into two parts: the first part simulates the PFH process, the second part simulates the downstream processing system that is common to both retorting methods. Because it was separated from the rest of the program, the PFH simulation must be provided with all parameters of the recycle gas coming from the downstream processing system as input. The flow rate and temperature of the recycle gas stream are calculated from the mass and energy balances in the PFH process. The correlations for calculating the appropriate specific heats of the solid and gaseous streams have been retained from the original program.

PFH Model

A generalized model for the PFH retort was proposed for incorporation into the computer program. The model is presented as 2 schemes in simplified drawings in Figure 6-92. The model is comprised of 3 fluidized beds: a preheat zone above the retort, a retorting zone, and a cooling zone below the retort. A hot gas recycle stream enters at the bottom of the retort and is

combined with the hot gas rising from the cooling zone below to provide heat for the retorting reactions. Because of the nature of a fluidized bed, the following assumption are made concerning thermal and mass parameters for the purpose of the study.

- The temperatures of the solids and gas in a fluidized bed are uniform throughout.
- The temperature of any streams exiting a fluidized bed are equal.
- Specific superficial gas velocities are required for proper fluidization.
- The residence times of the solids in each zone must be sufficient to insure attainment of thermal and kinetic equilibrium, reaction, and mass transfer.

In Scheme A, the hot product gas and oil from the retort (Stream 4) flow into the preheat zone, where the ambient temperature shale is preheated. The temperature of the vapor-phase products exiting the preheat zone (Stream 6) must be high enough to prevent any liquids from condensing on the shale in the preheat zone.

All the parameters of the Scheme A are listed in Table 6-37. A total of 11 unknown parameters marked "?" can be calculated according to the mass and energy balances in the three zones, as described later. The temperature of Stream 1 and the composition of both Streams 1 and 2 are finally determined from downstream system analysis.

Table 6-37. SPECIFIED AND UNKNOWN PARAMETERS FOR PFH RETORTING PROCESS
(Scheme A, see Figure 6-92)

<u>Stream No.</u>	<u>Mass Flow Rate</u>	<u>Temperature, °F</u>	<u>Composition</u>
A	Input	Input	Input
B	?*	Input (600-700)	?
C	=(D)	Input (950-1200)	=(D)
D	Input	Input (500-700)	Input
1	?	Input (100-150)	Input
1A	=(1)	=(D) (500-700)	=(1)
2	?	?	Input
3	=(1) + (2)	?	?
4	?	=(C) (950-1200)	?
6	?	=(B) (500-700)	?

* ? = Unknown parameter.

2. The oil yield is adjusted for particle size differences
3. The flows are scaled up to an appropriate commercial design basis (that is, 50,000 bbl/day or other).

The program can provide numerical results in terms of gas/oil production, pollutant emissions, and evaluations of both capital and operating costs according to various input data such as plant size, shale properties, and reaction parameters. However, in simulating the commercial operation, rigorous thermodynamic equilibrium calculations for the reaction, flash, and phase change, are not performed. The reaction parameters, production rate and the simple fixed split factors are given as input data based on an earlier conceptual plant design by Bechtel Group, Inc., and some experimental results. Therefore, such empiric or designed parameters could not be changed significantly for the purpose of parametric studies.

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PFH Model

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Because neither chemical reaction nor water evaporation occurs in the cooling zone, the mass flow rate (M) for shale Streams C and D and for gas Stream 1 and 1A do not change.

$$M_C = M_D \quad (6-23)$$

and

$$M_1 = M_{1A} \quad (6-24)$$

Therefore, the flow rate of Stream 1 can be determined by the energy balance around the cooling zone.

$$M_1 = \frac{M_C H_C - M_D H_D}{H_{1A} - H_1} \quad (6-25)$$

where enthalpies H_1 , H_{1A} , H_D and H_C are calculated based on the given temperature and composition of each stream, and the spent shale rate (M_D) is also given.

Preheating Zone: The discussion for Schemes A and B are presented separately below.

Scheme A:

Because the temperature and composition of each stream is given in Scheme A, the three unknown parameters (mass flow rates of output shale, input and output gas) can be calculated by the following three equations:

Material balance for shale stream:

$$M_B = M_A + M_W - \Delta M_W - \Delta M_S \quad (6-26)$$

Material balance for gas stream:

$$M_6 = M_4 + \Delta M_W + \Delta M_S \quad (6-27)$$

and energy balance for the system:

$$M_A H_A + M_W H_W + M_4 H_4 + \Delta Q = M_B H_B + M_6 H_6 \quad (6-28)$$

In Scheme B, the hot product gas and oil from the retort (Stream 4) flow out of the reactor in a separate stream. A hot recycle gas stream (Stream 5) provides the heat needed to preheat the feed shale in the preheat zone. This configuration is similar to that of the moving-bed retorting process; the product gas and oil from the retort (Stream 4) do not come in contact with the feed shale in the preheat zone, avoiding any condensation of oil on the raw shale. Table 6-38 lists the specified parameters for Scheme B. The temperatures of recycle gas (Streams 2 and 5) are provided so that the number of unknown parameters is the same as Scheme A. In the case that another parameter such as the temperature of Stream 3 or flow rate of Stream 2 or 5 is given, the temperature of the recycle gas can be calculated.

Table 6-38. SPECIFIED AND UNKNOWN PARAMETERS FOR PFH RETORTING PROCESS
(Scheme B, see Figure 6-92)

<u>Stream No.</u>	<u>Mass Flow Rate</u>	<u>Temperature, °F</u>	<u>Composition</u>
A	Input	Input	Input
B	?	Input (500-700)	?
C	=(D)	Input (950-1200)	=(D)
D	Input	Input (500-700)	Input
1	?	Input (100-150)	Input
1A	=(1)	=(D) (500-700)	=(1)
2	?	Input	Input
3	=(1) + (2)	?	?
4	?	=(C) (950-1200)	?
5	?	Input	Input
6	?	=(B) (500-700)	?

Material and Energy Balance

The calculation for the PFH retorting process is based on material and energy balances and is conceptually described as follows.

Cooling Zone: The calculations for the cooling zone are the same for Schemes A and B.

recycle gas (Stream 2 or Stream 3), or the flow rate of the recycle gas depending upon the case. It should be noted that the enthalpy of the gas and liquid flows in the streams described above is dependent not only upon temperature and pressure, but also stream composition. Therefore, iterative calculations are needed to make the mass balance calculation converge on a unique solution for each component.

The Minimum Fluidization Velocity

The minimum fluidization velocity (U_{mf}) of particles in a gas flow can be determined from the Ergun Equation:

$$U_{mf} = \left(\frac{\mu}{d_p g} \right) \cdot 42.86 \frac{1 - \epsilon_{mf}}{\phi} \left\{ \left[1 + \frac{\phi^3 \epsilon_{mf}^3 d_p^3 \rho_g \rho_s - \rho_g g_c}{1836.7 (1 - \epsilon_{mf})^2 \mu^2} \right]^{1/2} - 1 \right\} \quad (6-29)$$

where --

- μ = viscosity of gas or gas mixture, lb/ft s
- d_p = equivalent diameter of particles, ft
- ϕ = particle sphericity
- ϵ_{mf} = bed voidage
- ρ_s = density of particles, lb/ft³
- ρ_g = density of gas, lb/ft³
- g_c = gravitational constant, 32.17 ft/s² (9.8 m/s²)

Unit of U_{mf} is ft/s.

The Reynolds Number (Re_p) of a particle moving in a gas stream is given by --

$$Re_p = A (\sqrt{1 + B} - 1) \quad (6-30)$$

where --

$$A \equiv 42.86 \frac{1 - \epsilon_{mf}}{\phi}$$

$$B \equiv \frac{\phi^3 \epsilon_{mf}^3 d_p^3 \rho_g (\rho_s - \rho_g) g_c}{1836.7 (1 - \epsilon_{mf})^2 \mu^2}$$

In Scheme B, the hot product gas and oil from the retort (Stream 4) flow out of the reactor in a separate stream. A hot recycle gas stream (Stream 5) provides the heat needed to preheat the feed shale in the preheat zone. This configuration is similar to that of the moving-bed retorting process; the product gas and oil from the retort (Stream 4) do not come in contact with the feed shale in the preheat zone, avoiding any condensation of oil on the raw shale. Table 6-38 lists the specified parameters for Scheme B. The temperatures of recycle gas (Streams 2 and 5) are provided so that the number of unknown parameters is the same as Scheme A. In the case that another parameter such as the temperature of Stream 3 or flow rate of Stream 2 or 5 is given, the temperature of the recycle gas can be calculated.

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<u>Stream No.</u>	<u>Mass Flow Rate</u>	<u>Temperature, °F</u>	<u>Composition</u>
A	Input	Input	Input
B	?	Input (500-700)	?
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D	Input	Input (500-700)	Input
1	?	Input (100-150)	Input
1A	=(1)	=(D) (500-700)	=(1)
2	?	Input	Input
3	=(1) + (2)	?	?
4	?	=(C) (950-1200)	?
5	?	Input	Input
6	?	=(B) (500-700)	?

Material and Energy Balance

The calculation for the PFH retorting process is based on material and energy balances and is conceptually described as follows.

Cooling Zone: The calculations for the cooling zone are the same for Schemes A and B.

Figure 6-93. STRUCTURE OF THE PFH PLANT SIMULATION PROGRAM

In general, to calculate U_{mf} , d_p , ϕ , ϵ_{mf} , and ρ_s are given and ρ_g and μ are calculated based on the temperature, pressure and composition of the gas mixture within the particles are moving.

Computer Program

Modification of the computer program for a moving-bed retort simulation has been basically completed for the simulation of the PFH process. The major modifications made for the PFH retort simulation are as follows:

- Two process schemes proposed to simulate the PFH retort are incorporated in the program, as shown in Figure 6-91.
- The nominal temperatures in each fluidized-bed zone and corresponding material and heat balances have been specified for the PFH retorting process.
- A subroutine that calculates the U_{mf} of oil shale particles based on the pressure, temperature and the composition of the gas mixture in each zone has been made and incorporated into the program.
- Dimensions (diameter and height) of each fluidized bed zone are calculated based on the requirements for proper fluidization velocity and the residence time of shale particles in the bed.

The program structure is shown in Figure 6-93, the major outputs of this calculation in the retorting process are:

- Temperatures, mass flow rates and composition of each stream based on material and energy balances
- The ratio of recycle gas/retorting products in the retort zone
- Minimum fluidization velocities
- Diameter and height of each zone
- The saturation temperature and mole fraction of water vapor in the outlet recycle gas.

The products of the gas and oil retorted from oil shale are given in the existing program.

The residence time of solid particles and the mass flux in the fluidized beds are also given. Once the experimental results are obtained from other tasks, correlation could be developed for these parameters and incorporated into the program, as shown in Figure 6-93. The mass flux of shale through the retort has been specified as an input at 6000 lb/ft²/h (29302 kg/m²/h). Other values could be input for sensitivity analyses.

Figure 6-94. CALCULATION RESULTS FOR DIFFERENT ZONE TEMPERATURES

In general, to calculate U_{mf} , d_p , ϕ , ϵ_{mf} , and ρ_s are given and ρ_g and μ are calculated based on the temperature, pressure and composition of the gas mixture within the particles are moving.

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- The nominal temperatures in each fluidized-bed zone and corresponding material and heat balances have been specified for the PFH retorting process.
- A subroutine that calculates the U_{mf} of oil shale particles based on the pressure, temperature and the composition of the gas mixture in each zone has been made and incorporated into the program.
- Dimensions (diameter and height) of each fluidized bed zone are calculated based on the requirements for proper fluidization velocity and the residence time of shale particles in the bed.

The program structure is shown in Figure 6-93, the major outputs of this calculation in the retorting process are:

- Temperatures, mass flow rates and composition of each stream based on material and energy balances
- The ratio of recycle gas/retorting products in the retort zone
- Minimum fluidization velocities
- Diameter and height of each zone
- The saturation temperature and mole fraction of water vapor in the outlet recycle gas.

The products of the gas and oil retorted from oil shale are given in the existing program.

The residence time of solid particles and the mass flux in the fluidized beds are also given. Once the experimental results are obtained from other tasks, correlation could be developed for these parameters and incorporated into the program, as shown in Figure 6-93. The mass flux of shale through the retort has been specified as an input at 6000 lb/ft²/h (29302 kg/m²/h). Other values could be input for sensitivity analyses.

Figure 6-95. CALCULATED MINIMUM FLUIDIZATION VELOCITY (U_{mf}) OF OIL SHALE PARTICLES IN RECYCLE GAS MIXTURE

Curve 1 corresponds to the temperatures in the preheating zone and the cooling zone higher than the maximum selection -- 700°F (371°C). The left-side area of Curve 3 corresponds to the temperatures in the preheating zone and the cooling zone lower than the minimum selection -- 600°F (316°C). Therefore, only the area between Curves 1 and 3, and the line as $T(c) = 900^\circ\text{F}$ (482°C) corresponding to the minimum selected temperature in the retort zone is the feasible temperature range. Moreover, because the recycle gas temperature $T(2)$ has been limited to less than 1500°F (846°C), the feasible temperature range of each zone can be concluded as follows:

Preheating zone:	600° to 700°F
Retorting zone:	900° to 1000°F
Cooling zone:	600° to 700°F

Therefore, a basic temperature selection for Scheme A is recommended as follows:

Temperatures in preheating zone:	650°F
Temperatures in retorting zone:	950°F
Temperatures in cooling zone:	650°F

Thus, the range of temperature variation in each zone could be about $\pm 50^\circ\text{F}$ ($\pm 27.8^\circ\text{C}$). Since the effect of inlet gas temperature $T(1)$ on $T(2)$ is small and the variable range of $T(1)$ is limited in practice, a variation of $T(1)$ does not significantly impact the operating regime. However, this parameter selection could be varied depending upon given conditions.

U_{mf} Calculation

The minimum fluidization velocity (U_{mf}) is calculated in a subroutine in which the viscosity of gas mixture is computed based on gas temperature, pressure, and composition. A total of 24 gas components in the gas mixture can be considered in the calculation. Figure 6-95 shows the results of calculations made to determine the effects of gas temperature, pressure and particle size on the U_{mf} for the given recycle gas composition (H_2 -90%; CO -4%; CH_4 -4.8%, etc.). The U_{mf} is very slightly affected by gas temperature, but increases with particle size. The effect of pressure on U_{mf} is quite significant because of the dependence of gas density on pressure. In general, the U_{mf} decreases by about 30% as the pressure doubles. Particle size has an important effect on U_{mf} , as shown in the figure. However, since the actual oil shale particles have a rather broad size distribution, and the calculated particle size could be determined by different ways, the calculated U_{mf} can be significantly different. In order to ensure sufficient fluidization in the beds, the actual gas velocity is increased by 1.5 to 2.5 times the U_{mf} . For the present conditions, the actual gas velocities could be the same for two quite different particle sizes [for example, 0.09 inch and 0.20 inch (0.23 and 0.51 cm)] if the ensuring factors of fluidization operation for the two cases are taken as 2.5 and 1.5, respectively. Therefore, determination of the "calculated particle size" and the multiplying factor are essential for proper calculation of practical gas velocities in the PFH beds.

Subtask 6.4.2.a. Environmental Impacts: Potential Processing Effects

This subtask addresses 1) the environmental impacts of shale processing, and 2) the Federal and state laws, rules, and regulations that may affect the development of shale processing in the Eastern U.S.

Objectives

The objectives of this subtask are to provide an environmental assessment of a PFH facility and to compare the results with those for a thermal retorting process. For the purpose of the comparison, thermal retorting refers to the heating of oil shale in an inert atmosphere for pyrolysis in order to produce oil. These objectives can only be achieved by determining the quantity and quality of solid, liquid, and gaseous by-products from PFH and thermal retorting through the analysis of data available from the two retorting approaches.

Introduction

Declining world reserves of petroleum and natural gas have accelerated the development of technology to produce synthetic fuels from alternative sources. Synthetic fuels are obtained by converting a carbonaceous solid to liquid fuel and gas. In the United States, the most abundant naturally occurring materials suitable for this purpose are coal and oil shale. Of these two materials, the oil shale resource of this country is a more promising source of much needed liquid fuels and is found in both Eastern and Western regions. Most of the early major development efforts for recovering oil from oil shales have been concentrated in the Western deposits. However, recently the interest in the development of a commercial Eastern oil shale industry has increased substantially because of the following reasons.

1. Better water availability in the Eastern part of the U.S.
2. Presence of infrastructure and transportation systems.
3. Substantial recoverable resource.
4. Easily accessible reserves.

A number of retorting processes have been developed for processing the Eastern oil shales to produce oil. These processes can be divided into two broad classes, thermal and hydroretorting, and each will affect the environment in and around a commercial facility in a certain way. It would be of interest to compare the environmental concerns associated with the two classes of retorting processes. This will not only be helpful in assessing the environmental mitigation potential of each process, but the developers will also have an idea about their responsibilities regarding the protection of the environment.

The commercial processing of Eastern oil shales will involve massive amounts of raw materials, oil products, and wastes. One major concern for the emerging oil shale industry is the establishment of environmentally acceptable methods for the disposal of large volumes of processed shale. The processed shale contains potentially toxic trace elements such as those listed in

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Preheating zone:	600° to 700°F
Retorting zone:	900° to 1000°F
Cooling zone:	600° to 700°F

Therefore, a basic temperature selection for Scheme A is recommended as follows:

Temperatures in preheating zone:	650°F
Temperatures in retorting zone:	950°F
Temperatures in cooling zone:	650°F

Thus, the range of temperature variation in each zone could be about $\pm 50^\circ\text{F}$ ($\pm 27.8^\circ\text{C}$). Since the effect of inlet gas temperature $T(1)$ on $T(2)$ is small and the variable range of $T(1)$ is limited in practice, a variation of $T(1)$ does not significantly impact the operating regime. However, this parameter selection could be varied depending upon given conditions.

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The minimum fluidization velocity (U_{mf}) is calculated in a subroutine in which the viscosity of gas mixture is computed based on gas temperature, pressure, and composition. A total of 24 gas components in the gas mixture can be considered in the calculation. Figure 6-95 shows the results of calculations made to determine the effects of gas temperature, pressure and particle size on the U_{mf} for the given recycle gas composition (H_2 -90%; CO -4%; CH_4 -4.8%, etc.). The U_{mf} is very slightly affected by gas temperature, but increases with particle size. The effect of pressure on U_{mf} is quite significant because of the dependence of gas density on pressure. In general, the U_{mf} decreases by about 30% as the pressure doubles. Particle size has an important effect on U_{mf} , as shown in the figure. However, since the actual oil shale particles have a rather broad size distribution, and the calculated particle size could be determined by different ways, the calculated U_{mf} can be significantly different. In order to ensure sufficient fluidization in the beds, the actual gas velocity is increased by 1.5 to 2.5 times the U_{mf} . For the present conditions, the actual gas velocities could be the same for two quite different particle sizes [for example, 0.09 inch and 0.20 inch (0.23 and 0.51 cm)] if the ensuring factors of fluidization operation for the two cases are taken as 2.5 and 1.5, respectively. Therefore, determination of the "calculated particle size" and the multiplying factor are essential for proper calculation of practical gas velocities in the PFH beds.

Scope and Methods

In order to compare the potential environmental effects of the PFH process with thermal retorting, a study based upon the published data was initiated. The necessary data were sought from the following sources.

1. Environmental databases. The available environmental databases were accessed through computerized literature search to identify publications containing data on environmental effects, which could be used for comparing the two processes
2. Institute of Gas Technology (IGT). Since the literature search did not identify any published data on the PFH process, IGT provided some useful information from their retorting experiments.
3. Personal contacts. Some participants of 1989 Eastern Oil Shale Symposium including active researchers and professionals involved with the operation of commercial-sized retorting facilities were contacted in order to obtain information from thermal retorting processes.
4. Kentucky Center for Applied Energy Research (KCAER). Most of the data from thermal retorting process were obtained from the publications of KCAER, which has carried out extensive research in this area.

Some leaching experiments were performed by TTU (Cookeville, Tennessee), on Indiana New Albany shale samples processed by PFH. These samples were provided by IGT. The data from these experiments were used where appropriate.

The literature search identified very few publications that provided the necessary data from thermal retorting. Wherever the data from PFH was not available, the information from moving-bed hydroretorting was used for making the comparison.

Results and Discussion

Each operation of a commercial Eastern oil shale industry to produce oil will have potential impacts on the environment. These impacts should be addressed individually and collectively to ensure their compliance with the applicable Federal and State laws and regulations. The environmental assessment of these impacts must be based upon available laboratory data, the published literature, a knowledge of wastewater treatment processes, and the laws and regulations, because of the absence of any track record on this comparatively new industry. The available data are presented in the following paragraphs.

Solids

Solids present potential environmental problems during each phase of handling and processing of oil shales. Some of the major problem areas are discussed below.

Table 6-1 (Ag, As, Ba, Cd, Cr, Pb, Hg, and Se), which may potentially migrate into the environment. Agarwal¹ estimates that even if one-half of the planned oil shale production in the U.S. occurs, about 245 million metric tons of processed shale will be disposed each year.

Most disposal scenarios call for the construction of compacted embankments, which may cover many hectares and extend hundreds of meters in depth. Retorted oil shale materials disposed of in these configurations will be in contact with aqueous percolates from precipitation, run-off, and possibly ground water sources, unless proper measures are taken to avoid such contacts. These percolates, commonly referred to as leachates, may contain elevated levels of certain objectionable elements and should be characterized in order to reduce their environmental impacts.

The characterization of these leachates and the process water generated during the retorting process is a necessary first step in assessing if, and to what extent, water quality and other environmental problems may arise in the development of a commercial Eastern oil shale industry. The leaching characteristics of raw shale, retorted shale, and other associated materials will determine the level of treatment necessary prior to water discharge, and the long-range hazards such materials may present to surface and ground water quality.

Shale processing activities will also have potential impacts on the atmosphere. These impacts may be a result of process emissions from different stages of operation such as mining, crushing, transportation, and retorting. The gaseous emissions pertain to particulates, sulfur dioxide, nitrogen oxides, carbon monoxide, hydrocarbons, and photochemical oxidants and other compounds.

Particulates result from all stages of oil shale industry operations. When released into atmosphere, they may increase the particulate load in the ambient air beyond allowable limits.

Hydrogen sulfide and sulfur dioxide are major sulfur compounds resulting from shale retorting. Each is of concern because of its toxic effects. They are regulated by State and Federal emission standards as well as by the ambient air regulations and are one of the significant pollution control problems faced by U.S. industry.

Nitrogen oxides result from the elemental nitrogen present in the oxidizing medium of thermal retorting. The emission of these substances to the atmosphere is undesirable from a physiological point of view. They can also provoke chemical reactions in the atmosphere that may result in the formation of photochemical oxidants.

Hydrocarbons and carbon monoxide can be present in the gas stream of any incomplete combustion process. Significant concentrations of these compounds are expected from thermal retorting processes because of the incomplete combustion of carbon present in the oil shale.

Another potential problem associated with the retorting of oil shale is that of trace metal emissions. The retorting operations can release trace metals into the environment in two ways; direct volatilization and particulate carry-over.

Table 6-40. CHEMICAL ANALYSES OF FEEDSTOCK, HYDRORETORTED,
AND THERMALLY RETORTED INDIANA NEW ALBANY SHALE

Element	Feedstock	Hydroretorting wt %	Hydroretorting Recovery, %	Thermal wt %	Thermal Recovery, %
C	12.17	2.65	78	6.38	48
H	1.49	0.04	97	0.25	83
N	0.39	0.01	97	0.31	21
S	5.03	3.03	40	4.00	20
Moisture	1.25	3.60	--*	0.76	39
Ash	79.85	94.02	--	87.90	--
SiO ₂	61.55	63.89	--	63.05	--
TiO ₂	0.79	0.71	10	0.81	--
Al ₂ O ₃	13.60	12.16	11	14.02	--
Fe ₂ O ₃	10.48	11.06	--	10.13	3
CaO	1.96	1.09	44	1.62	17
MgO	1.60	1.36	15	1.62	--
K ₂ O	4.04	3.56	12	4.13	--
Na ₂ O	0.60	0.61	--	0.55	8
P ₂ O ₅	0.13	0.12	8	0.13	--
		----- ppm -----			
Ba	442	398	10	439	0.7
Co	32	33	--	32	--
Cr	98	85	13	92	6
Cu	96	96	--	106	--
Mo	171	166	3	163	5
Ni	117	111	5	110	6
Pb	121	109	10	118	2
V	231	199	14	233	--
Zn	182	66	64	150	18

* Indicates more than 100% recovery.

lower carbon content. The reduced risk of spontaneous combustion will make the disposal of hydroretorted shale more environmentally safe than the thermally retorted shale.

During the retorting process, the sulfur content of the raw shale is reduced as it is transferred to oil and gaseous products. As shown in Table 6-40, thermally retorted shale contains 20% more sulfur by weight than the hydroretorted shale. Since the sulfur concentration of the spent shale will be related to acid-production potential, thermally retorted shale will exhibit a greater potential for the generation of acidic leachates if the waste pile comes in contact with water. By comparison, the spent shale from hydroretorting will mitigate this environmental impact because of a lower content of sulfur than thermally retorted shale.

The concentrations of the major elements in the spent shales from both thermal and hydroretorting are also presented in Table 6-40. These concentra-

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The characterization of these leachates and the process water generated during the retorting process is a necessary first step in assessing if, and to what extent, water quality and other environmental problems may arise in the development of a commercial Eastern oil shale industry. The leaching characteristics of raw shale, retorted shale, and other associated materials will determine the level of treatment necessary prior to water discharge, and the long-range hazards such materials may present to surface and ground water quality.

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Another potential problem associated with the retorting of oil shale is that of trace metal emissions. The retorting operations can release trace metals into the environment in two ways; direct volatilization and particulate carry-over.

potential of some selected trace elements using two leaching tests, EP Toxicity, and ASTM-B. The data from the two aforementioned processes are given in Table 6-41. The table also shows the Resource Conservation and Recovery Act (RCRA) limits for the elements studied.

Table 6-41. COMPOSITION OF RETORTED SHALE LEACHATES FROM INDIANA NEW ALBANY SHALE PROCESSED BY THERMAL RETORTING AND HYTORT PROCESS

Constituent	Thermal Retorting		Hydroretorting Process		RCRA Limits
	B	EP	B	EP	
pH	4.50	3.48	5.00	5.17	--
	-----		mg/L	-----	
Ag	0.05	0.04	0.15	0.13	5
As	<0.005	0.014	<0.005	0.026	0.5
Ba	0.23	0.13	0.29	0.16	100
Cd	0.02	0.018	<0.001	<0.001	1
Cr	0.08	0.06	<0.03	<0.03	5
Hg	-----		<0.0005	-----	0.2
Pb	0.008	0.035	<0.0005	<0.0005	5
Se	-----		<0.005	-----	1

B = ASTM-B procedure for determining leachate concentrations in aqueous samples.

EP = EP Toxicity test.

The analysis of the data indicates quite a difference between the leachate pH values from the hydroretorted samples and those from thermal retorting. The hydroretorted samples exhibit much higher pH values than the corresponding values for the thermal retorted samples. This could be due to highly reducing conditions encountered in the hydroretorting process, which will result in the conversion of pyrite (FeS_2) to pyrrhotite (FeS) or possibly even elemental iron, with a consequent reduction in the acid-producing potential of the hydroretorted spent shales.

The leachability of the selected elements does not indicate any favorable trend for either retorting technology. The concentrations of Cd, Cr, and Pb are lower in the leachates from hydroretorted samples than thermal retorted samples. However, an opposite trend was observed for Ag, As, and Ba, as the concentrations of these elements were higher for the hydroretorted leachates.

EP toxicity studies show that both the hydroretorting and thermal retorting processes will produce a spent shale meeting RCRA limits specified by the U.S. EPA. Therefore, leaching problems should not be expected from the disposal of the shale retorted by either process.

Table 6-42 provides the data from the leachability studies performed on Indiana shales processed by thermal retorting and PFH. The data from thermal retorting were reported by Robl and Koppenaal,⁷ whereas the PFH processed shale samples were extracted at TTU, Tennessee. The ASTM-A extraction procedure was used to collect the leachates.

tions are about the same for both spent shales thus, if concentration is the controlling parameter, the two will affect the disposal environment in almost the same manner. Hydroretorting might have a slight edge over thermal retorting regarding the concentrations of iron oxide. Taylor *et al.*⁵ recommended that iron oxides be avoided in retorting because they react rapidly with H_2S to form FeS , which becomes a source of SO_2 during combustion. The data in Table 6-40 indicates a slight increase in the concentration of Fe_2O_3 during hydroretorting, whereas some Fe_2O_3 was transferred during thermal retorting.

The stability of a spent shale disposal pile will depend on the characteristics of the shale particles. Gerhart and Holtz⁴ found that high retorting temperatures produce a retorted shale with natural pozzuolanic properties, whereas, free-carbon rich retorted shales resulting from low temperature retorting processes demonstrate very little or no pozzuolanic properties. Therefore, the PFH process, in which the retorting takes place in a temperature range of 900° to 1200°F (482° to 649°C), will have a distinct advantage over other low temperature retorting processes, operating at 500° to 850°F (260° to 454°C) temperatures, in that the PFH processed shale will result in a more stable disposal pile. This disposal pile will be subjected to a lesser degree of erosion and subsequently a lower quantity of particulates will be released to the surrounding environment.

The fine grained, high temperature retorted shales would promote more growth of acicular crystals of calcium aluminum sulfate between the contacts of shale fragments.⁴ This phenomenon will result in higher strengths and reduced permeabilities in the disposal piles. This fact also favors PFH over other retorting processes, which utilize coarser particle size and low retorting temperatures.

All surface retorting processes require crushed raw shale feed of predetermined size ranges. The smaller particles from a crushed and sized batch of feedstock, which cannot be fed to the retort, must be removed and discarded. In most retorting systems, oil shale fines consist of particles from 1/2 to 1/8-inch (1.3 to 0.3 cm) in size, with a common size of around 1/4 inch (0.64 cm).⁶ The fines fraction of coarse particle processes, which represents about 10% of the feedstock poses two problems. First is the mining and handling of larger quantities of raw shale, which can increase the particulate loading on the ambient air. Second, the disposal of this waste material can harm the environment by leaching of toxic substances and acid mine drainage because raw shale has been found to be much more reactive than retorted shale. Since PFH utilizes a fine particle size consist (-60+100 mesh), it has a potential to mitigate the effects of these two problems.

Leaching

Leaching studies of spent shales are helpful in characterizing the aqueous effluents generated as a result of contact with various oil shale waste materials and identifying the water quality problems that may arise from the development of an Eastern oil shale industry. Robl and Koppenaal⁷ reported the leachability data for the Indiana spent shale processed by both thermal retorting and hydroretorting from the laboratory tests designed to simulate the physico-chemical conditions that will be encountered in a particular disposal configuration. This data compares the leachability

Table 6-43. RAW SHALE AND PRODUCT OIL ANALYSES

Process Shale	<u>KENTORT II</u> <u>Ohio (Cleveland)</u>		<u>Hydroretorting</u> <u>Indiana (New Albany)</u>
Oil Recovered, GPT	17.7		24.1
GPT/wt % Organic Carbon	1.06		1.95
Shale Analysis			
Carbon	16.7		12.37
Hydrogen	2.0		1.54
Nitrogen	0.7		0.45
Sulfur	1.7		4.67
Ash	74.5		75.14
Oil Analysis			
Sulfur	1.60*	1.73**	1.44
Nitrogen	0.75	0.82	2.03
Pour Point, °F	15	0	-5

* Non-recycle mode of operation.

** Solids-recycle mode of operation.

the conclusion that for the same amount of oil produced, hydroretorting will result in a lower quantity of spent shale, which will have to be disposed of in an environmentally safe manner, and will thus be an environmental problem of a lesser degree.

Table 6-44 presents percent carbon distribution in product oil, gas, spent shale, and aqueous phase for both the KENTORT II and hydroretorting processes. In the hydroretorting process, the percentage of carbon that goes to oil production is about 71%, whereas the thermal process converts about 42% to 46%. Similarly, the percentage of carbon converted to gas and remaining in the spent shale is higher for the thermal process. The carbon balance does not total 100% for the thermal process, because the yields were not reconciled as were the hydroretorting values.

Table 6-44. CARBON DISTRIBUTION

<u>Item</u>	<u>KENTORT II</u>		<u>Hydroretorting</u>
	<u>(Non-recycle)</u>	<u>(Recycle)</u>	
Carbon Distribution, wt %			
Oil	45.9	42.3	71.4
Gas	15.9	9.9	12.4
Spent Shale	29.5	38.7	16.2
Aqueous Phase	<u>2.5</u>	<u>1.8</u>	<u>--</u>
Total	93.9	92.7	100.0

tions are about the same for both spent shales thus, if concentration is the controlling parameter, the two will affect the disposal environment in almost the same manner. Hydroretorting might have a slight edge over thermal retorting regarding the concentrations of iron oxide. Taylor *et al.*⁵ recommended that iron oxides be avoided in retorting because they react rapidly with H_2S to form FeS , which becomes a source of SO_2 during combustion. The data in Table 6-40 indicates a slight increase in the concentration of Fe_2O_3 during hydroretorting, whereas some Fe_2O_3 was transferred during thermal retorting.

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Leaching

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- Longer potential exposure of the general population to the pollutants than the workers.
- Reactions in the atmosphere to produce more toxic or undesirable compounds.
- Consideration of nuisance in setting the limits rather than the highest concentrations for which no detrimental effects are believed to occur.

Other Gases

Product gas analyses from the processing of Indiana shale by the Allis-Chalmers Roller Grate Retort Process and PFH are shown in Table 6-45. These values are presented in mole percent and on an H₂S-free basis. The data indicate that PFH contains a high concentration of hydrogen, which is recovered and reused for retorting, whereas the Allis-Chalmers process results in quite high values for CO, CO₂, and higher hydrocarbons compared with those from the PFH process.

Table 6-45. OFF-GAS ANALYSES FROM PFH AND ALLIS-CHALMERS RETORTING PROCESSES*

Component *	PFH	Allis-Chalmers
	----- mol % -----	-----
H ₂	89.44	30.03
CO	0.81	4.90
CO ₂	0.24	7.41
CH ₄	5.50	26.26
C ₂ 's	2.34	12.06
C ₃ 's	1.04	6.90
C ₄ 's	0.38	5.03
C ₅ 's	0.13	7.41
C ₆ 's	0.12	NA

* H₂S-free basis.

Water

Table 6-46 presents the data on the metals found in the process water resulting from the processing of Eastern oil shale by both moving-bed hydroretorting and thermal retorting. A rational comparison of the two is difficult because different shales were used as feedstocks.

Indiana New Albany shale was used for hydroretorting whereas the KENTORT II process utilized Kentucky Cleveland shale. In the thermal process, water analyses were conducted on waters collected in the water-cooled heat exchanger where the bulk of the fluidizing steam was condensed.⁸ The reactor was operated in both a non-recycle mode, in which the heat for pyrolysis was provided by the fluidizing media and an external coaxial furnace, and in a solids-recycle mode where a portion of the pyrolysis heat was provided by hot gasified shale. For the thermal process, the metal concentrations are an average of solids-recycle runs. In case of moving-bed hydroretorting, the

Gases

Retorting operations involve the emission of various compounds, which can find their way to the atmosphere and damage the environment. The following section describes potential emission of gases to the environment.

Sulfur Compounds

Emissions of sulfur to the atmosphere from processing of Eastern oil shales will be a major concern for the industry developers and environmentalists because of the relatively high sulfur content of shale. During hydroretorting, about 40% of the sulfur is mobilized to oil and retort gas, whereas the other 60% remains in the spent shale. Thermal retorting, however, converts about 20% of the sulfur to oil and other products, and the remaining 80% stays in the processed shale.

Carter *et al.*⁹ reported that the KENTORT II will convert about 70% of the sulfur to H_2S under the mildest conditions and that a portion of the remaining sulfur will be converted to SO_2 because of the oxidizing conditions under which retorting is carried out. Of these two forms of sulfur, (H_2S or SO_2), H_2S is easier to recover than SO_2 . It is anticipated that the steam/pyrrhotite reactions in the gasification stage of the thermal process will be enhanced in order to convert a substantial amount of sulfur from the solids to H_2S . Theoretically, high temperature pyrolysis in the gasifier accounts for a large portion of H_2 production in accordance with the following reaction:

Also, the conversion of FeS to Fe_3O_4 is considered as a source of H_2 .

In other words, reducing conditions are to be introduced into the gasification stage of the thermal process in order to increase the production of H_2S . In the HYTORT process, pyrite is the main feed sulfur species, which decomposes to FeS during retorting and contributes to sulfur conversion and H_2S production. In this way, hydroretorting results in the occurrence of more than 99% of the product-gas sulfur in the form of H_2S . No SO_2 is produced during retorting. For clean up purposes, handling of H_2S is safer than SO_2 because of the difference in toxicity limits for the two compounds, which have been established by the Occupational Safety and Health Administration (OSHA) as 10 parts per million (ppm) and 2 ppm (time weighted average), respectively, for long-term exposure to workers in the working environment.¹⁰ Also, the American Conference of Governmental Industrial Hygienists recommended in 1989 that the concentrations for H_2S and SO_2 , exposure be limited to 10 and 2 ppm, respectively.¹¹ Since both of these references indicate that SO_2 is more toxic than H_2S , hydroretorting will have a distinct advantage over thermal retorting because of no production and no subsequent handling of SO_2 . The potential release of SO_2 to the environment during the processing of the shale also poses a significant environmental hazard as evidenced by the extremely low concentrations permissible in the ambient air. Some important considerations used in establishing the permissible ambient air concentrations are:

2. Leaching and run-off from a smaller quantity of spent shale reduces the magnitude of potential environmental effects.
3. The lower carbon content of hydroretorted shale reduces the possibility of auto-combustion in a spent shale pile.
4. Low temperature retorting, which is typical of thermal processes, increases the potential for spontaneous ignition and emission of volatiles from the spent shale pile.
5. Spent shale from thermal retorting contains 20% more sulfur than that from hydroretorting. Thus, the potential for producing acidic leachate is greater when thermal processing is used.
6. Major elements in the spent shale from both thermal and hydroretorting are only slightly mobilized. Thus, the spent shale from each process will have about the same concentrations of these elements.
7. Shales hydroretorted at 900° to 1200°F (482° to 649°C) should exhibit pozzuolanic properties, which will result in a more stable and erosion resistant disposal pile.
8. Utilization of fines in the PFH process mitigates leaching problems that would occur if raw shale fines are rejected from the process that cannot utilize them.
9. Results from EP toxicity extractions of both hydroretorted and thermal retorted shales show that RCRA limits will be met and there will be no significant leaching problems.
10. Results from the ASTM-A extractions, which simulates rainwater, indicate that the water coming in contact with hydroretorted shale will exhibit a pH that is in the range specified by EPA for wastewater disposal. Shale leachate from the thermal process exhibits a lower pH.
11. Sour water from both hydroretorting and thermal retorting will require treatment before discharging or recycling.
12. The production of H₂S in the hydroretorting process has two significant advantages over the production of SO₂ by the thermal process; (a) H₂S is more easily removed from the gas stream, and (b) H₂S is less toxic than SO₂.

References

1. Agarwal, A. K., "Assessment of Solid Waste Characteristics and Control Technology for Oil Shale Retorting," EPA/600/7-86/019, Research Triangle Park, North Carolina, 1986.
2. Shogren, R., and S. D. Taylor, "Kentucky's Proposed Oil Shale Regulatory Program," Synthetic Fuels from Oil Shale II--Symposium Papers, Institute of Gas Technology, Chicago, Illinois, 1981, p. 503-514.

Gases

Retorting operations involve the emission of various compounds, which can find their way to the atmosphere and damage the environment. The following section describes potential emission of gases to the environment.

Sulfur Compounds

Emissions of sulfur to the atmosphere from processing of Eastern oil shales will be a major concern for the industry developers and environmentalists because of the relatively high sulfur content of shale. During hydro-retorting, about 40% of the sulfur is mobilized to oil and retort gas, whereas the other 60% remains in the spent shale. Thermal retorting, however, converts about 20% of the sulfur to oil and other products, and the remaining 80% stays in the processed shale.

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In other words, reducing conditions are to be introduced into the gasification stage of the thermal process in order to increase the production of H_2S . In the HYTORT process, pyrite is the main feed sulfur species, which decomposes to FeS during retorting and contributes to sulfur conversion and H_2S production. In this way, hydroretorting results in the occurrence of more than 99% of the product-gas sulfur in the form of H_2S . No SO_2 is produced during retorting. For clean up purposes, handling of H_2S is safer than SO_2 because of the difference in toxicity limits for the two compounds, which have been established by the Occupational Safety and Health Administration (OSHA) as 10 parts per million (ppm) and 2 ppm (time weighted average), respectively, for long-term exposure to workers in the working environment.¹⁰ Also, the American Conference of Governmental Industrial Hygienists recommended in 1989 that the concentrations for H_2S and SO_2 , exposure be limited to 10 and 2 ppm, respectively.¹¹ Since both of these references indicate that SO_2 is more toxic than H_2S , hydroretorting will have a distinct advantage over thermal retorting because of no production and no subsequent handling of SO_2 . The potential release of SO_2 to the environment during the processing of the shale also poses a significant environmental hazard as evidenced by the extremely low concentrations permissible in the ambient air. Some important considerations used in establishing the permissible ambient air concentrations are:

Subtask 6.4.2.b. Environmental Impacts: Laws and Regulations

Objective

The objective of this work was to assemble the environmental laws and regulations on water, air, solid waste, hazardous waste, and mining that were deemed to directly or indirectly impact the siting of an oil shale processing plant. The study included federal and state laws and regulations for the states of Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee. The compilation of this report is categorized into 1) purpose of the law, 2) associated rules and regulations, 3) legislative history of the law, and 4) state agency administering the law and implementing the regulations. A list of contacts/addresses for the responsible federal and state agencies is also provided.

Methods and Sources

The federal environmental regulations, standards, and guidelines set forth by various federal agencies, especially the Environmental Protection Agency (EPA), are either adopted or modified by state governments on the basis of their unique geological location, available natural resources, population, and other public interests. Therefore, only the sections deemed important in identifying criteria for siting an oil shale processing plant are cited in this subtask. The first enactment dates of the federal and state legislatures are only shown in the report because sections of these public laws and regulations are amended from time to time. The numerical requirements of specific standards and guidelines are generally excluded. In order to assure that the information presented is complete and consists of the most recent amended environmental legislature, copies of the document were sent to various state agencies for verification.

The findings of this report are essentially extracted directly from the body of the state laws, regulations, or legal publications of the state agencies that are responsible for implementing and monitoring them. Personal communications through telephone or mail with various federal and state authorities were made in order to update and clarify the information.

Federal legislation, which is termed primary federal legislations in this report, is believed to be most applicable and has a direct impact on siting an oil shale processing plant. Similarly, secondary federal legislation is that believed to have a significant impact on siting the plant. Most of the literature concerning the primary and secondary federal laws are generally available to this research; however, most of their corresponding regulations need to be obtained from the responsible agencies.

State governments, in most instances, have been given the responsibility to implement federal legislation within their borders. Most of the state legislative literature is either obtained from the legal publications or state agencies that are responsible for their promulgation. It is common to find that the environmental laws and regulations of many states overlap and may not be consistent with the federal guidelines.

3. Rex, Jr., Raymond C. and William C. S. Hu, "A Comparison of Hydroretorting and Thermal Retorting Facilities for the Processing of Eastern Oil Shale," 1986 Eastern Oil Shale Symposium, Kentucky Energy Cabinet Laboratory, Lexington, Kentucky, p. 185-192.
4. Gerhart, Phil C., and Wesley G. Holtz, "Disposal Concepts as Related to Retorted Shale Properties," 1981 Eastern Oil Shale Symposium, Institute for Mining and Minerals Research, University of Kentucky, Lexington, Kentucky, p. 87-97.
5. Taylor, R. W., C. J. Morris, and T. Coburn, "Rates of Chemical Reactions That Fix the Distribution of Sulfur in Processing Eastern Oil Shales". 1988 Eastern Oil Shale Symposium, Institute for Mining and Minerals Research, University of Kentucky, Lexington, Kentucky, p. 147-161.
6. Park, U-Sun, Chang-Yul Cha, James Winter and James Gresham, "Utilization of Oil Shale Process By-Products and Its Economics," 1982 Eastern Oil Shale Symposium, Institute for Mining and Minerals Research, University of Kentucky, Lexington, Kentucky, p. 203-212.
7. Robl, Thomas L. and David W. Koppenaal, The Chemical and Engineering Properties of Eastern Oil Shale, Kentucky Center for Energy Research Laboratory, Lexington, Kentucky, 1982.
8. Personal communication with IGT personnel, 1989.
9. Carter, S. D., D. N. Taulbee, T. L. Robl and A. Rubel. The Development of the KENTORT II Process for Eastern U.S. Oil Shale, Progress Report for the Period of October 1, 1988-December 31, 1988, Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky, 1989.
10. Occupational Safety and Health Administration, Occupational Safety and Health Standards for General Industry, Commerce Clearing House, Inc., Chicago, Illinois, 1989, p. 429, 446.
11. American Conference of Governmental Industrial Hygienists, Threshold Limit Values for Chemical Substances in Workroom Air, ACGIH, Cincinnati, Ohio, 1989.
12. Mensinger, M. C., M. J. Roberts, D. M. Rue and F. S. Lau, "Environmental Data from Moving-bed Hydroretorting of Three Eastern Oil Shales" 1988 Eastern Oil Shale Symposium, Institute for Mining and Minerals Research, University of Kentucky, Lexington, Kentucky, p. 133-146.

29WP/61090T6-4a/RPP

References

1. Public Law 91-190.
2. CFR Title 40, Part 6.
3. CFR Title 40, Parts 1500 et. seq.
4. Environment Reporter, Federal Laws, Vol. 2, 1989.

Resource Conservation and Recovery Act of 1976

Law. The Resource Conservation and Recovery Act (RCRA) evolved from the 1965 Solid Waste Disposal Act (P.L. 89-272). Congressional intent upon enactment of RCRA was "to provide technical and financial assistance for the development of management plans and facilities for the recovery of energy and other resources from discarded materials, for the safe disposal of discarded materials, and to regulate the management of hazardous waste." Sections of the Act that could apply to oil shale producers, in the event that the spent shale is determined to be hazardous, are:

Subtitle A:

- Section 3001: Identification and Listing of Hazardous Waste
- Section 3002: Standards Applicable to Generators of Hazardous Waste
- Section 3003: Standards Applicable to Transportation of Hazardous Waste
- Section 3005: Permits for Treatment, Storage, or Disposal of Hazardous Waste
- Section 3010: Effective Date
- Section 3013: Monitoring, Analysis, and Testing.

Subtitle B:

- Section 2001: Office of Solid Waste

Regulations. Specific regulations for RCRA are set forth in the Code of Federal Regulations (CFR) Title 40, Parts 260-268.

- 40 CFR 260: EPA General Regulations for Hazardous Waste Management
- 40 CFR 261: EPA Regulations for Identifying Hazardous Waste
- 40 CFR 262: EPA Regulations for Hazardous Waste Generator
- 40 CFR 264: EPA Regulations for Owners and Operators of Permitted Hazardous Waste Facilities
- 40 CFR 265: EPA Interim Standards for Owners and Operators of Hazardous Waste Facilities
- 40 CFR 268: EPA Regulations on Land Disposal Restrictions.

The recent amendment of the Bevill exclusion (Representative Tom Bevill, Alabama) impacts the siting of an oil shale production plant by amending 40 CFR 261.4(b)(7). This change excludes coal from its previous regulatory control since it is a solid waste created from the extraction, beneficiation, and processing of ores and minerals. Gasifier ash and processed wastewater from coal gasification are conditionally retained as excluded solid waste from the processing of ores and minerals subject to further data evaluation. Final boundaries for "conditionally" solid waste are to be set forth by EPA. Specific characteristics of a substance deemed hazardous include ignitability, corrosivity, reactivity, and toxicity. Other regulated substances pertaining

3. Rex, Jr., Raymond C. and William C. S. Hu, "A Comparison of Hydroretorting and Thermal Retorting Facilities for the Processing of Eastern Oil Shale," 1986 Eastern Oil Shale Symposium, Kentucky Energy Cabinet Laboratory, Lexington, Kentucky, p. 185-192.
4. Gerhart, Phil C., and Wesley G. Holtz, "Disposal Concepts as Related to Retorted Shale Properties," 1981 Eastern Oil Shale Symposium, Institute for Mining and Minerals Research, University of Kentucky, Lexington, Kentucky, p. 87-97.
5. Taylor, R. W., C. J. Morris, and T. Coburn, "Rates of Chemical Reactions That Fix the Distribution of Sulfur in Processing Eastern Oil Shales". 1988 Eastern Oil Shale Symposium, Institute for Mining and Minerals Research, University of Kentucky, Lexington, Kentucky, p. 147-161.
6. Park, U-Sun, Chang-Yul Cha, James Winter and James Gresham, "Utilization of Oil Shale Process By-Products and Its Economics," 1982 Eastern Oil Shale Symposium, Institute for Mining and Minerals Research, University of Kentucky, Lexington, Kentucky, p. 203-212.
7. Robl, Thomas L. and David W. Koppenaal, The Chemical and Engineering Properties of Eastern Oil Shale, Kentucky Center for Energy Research Laboratory, Lexington, Kentucky, 1982.
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10. Occupational Safety and Health Administration, Occupational Safety and Health Standards for General Industry, Commerce Clearing House, Inc., Chicago, Illinois, 1989, p. 429, 446.
11. American Conference of Governmental Industrial Hygienists, Threshold Limit Values for Chemical Substances in Workroom Air, ACGIH, Cincinnati, Ohio, 1989.
12. Mensinger, M. C., M. J. Roberts, D. M. Rue and F. S. Lau, "Environmental Data from Moving-bed Hydroretorting of Three Eastern Oil Shales" 1988 Eastern Oil Shale Symposium, Institute for Mining and Minerals Research, University of Kentucky, Lexington, Kentucky, p. 133-146.

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Clean Air Act of 1963

Law. The Clean Air Act (CAA) was enacted in 1963 when the Department of Health, Education, and Welfare was authorized by Congress to study air pollution. The act was significantly restructured in 1970 (P.L. 95-95 and P.L. 95-190) posing more stringent levels for ambient air quality and emission levels.

The original purpose of the act was to restrict emissions of the seven most common air pollutants: 1) carbon monoxide, 2) hydrocarbon, 3) lead, 4) nitrogen dioxide, 5) ozone, 6) particulate, and 7) sulfur dioxide. As of now, the purpose of the CAA is to protect and enhance the quality of the nation's air resources so as to promote the public health and welfare and the productive capacity of its population by preventing and controlling air pollution.

The major titles of the present CAA that impact the siting of an oil shale plant are:

Title I, Part A:

Section 107: Air Quality Control Region
Section 108: Air Quality Criteria and Control Technique
Section 109: National Ambient Air Quality Standards (NAAQS)
Section 110: State Implementation Plans (SIP)
Section 111: National Standards of Performance for New Stationary Sources (NSPS)
Section 112: National Emission Standards for Hazardous Air Pollutants (NESHAP)

Title I, Part C:

Section 160: Prevention of Significant Deterioration (PSD) of Air Quality.

The CAA has several amendments presently being debated in Congress which, if passed, may be applicable to the siting of a plant.

Regulations. While standards are promulgated and administered by the EPA, individual states have the responsibility for maintaining the air quality standards. The most pertinent federal regulations are:

40 CFR 50: EPA Regulations on National Primary and Secondary Ambient Air Quality Standards
40 CFR 60: Dates for Determining Applicability of Clean Air Act New Source Performance Standards
40 CFR 60: EPA Regulations and Standards of Performance for New Stationary Sources
40 CFR 61: EPA Regulations on National Emission Standard for Air Pollution.

Legislative History. The CAA has been amended to include new and/or changed authority. In addition, some amendments use the CAA as a vehicle to establish other federal statutes. In any event, each amendment should be studied to determine its impact on the siting of an oil shale plant.

to oil shale facilities could possibly include spent catalysts and processed shale.

Industries that generate, transport, treat, store, or dispose of waste removed from temporary exclusion by 40 CFR, Part 261, Subpart C, will be required to notify either EPA or an authorized state of these activities pursuant to Section 3010 of RCRA.

Legislative History. The RCRA has been amended to include new and/or changed authority. In addition, some amendments use the RCRA as a vehicle to establish other federal statutes (acts); i.e., the Solid Waste Disposal Act. In any event, each amendment should be studied to determine its impact on the siting of an oil shale plant.

The legislative history of the RCRA is as follows:

Enacted by PL 94-580 in 1976, Resource Conservation and Recovery Act
Amended by PL 95-609 in 1978, Quiet Communities Act
Amended by PL 96-463 in 1980, Used Oil Recycling Act
Amended by PL 96-482 in 1980, Solid Waste Disposal Act
Amended by PL 96-510 in 1980, Comprehensive Environmental Response, Compensation, and Liability Act
Amended by PL 97-272 in 1982
Amended by PL 97-375 in 1982, Congressional Reports Elimination Act
Amended by PL 98-45 in 1983
Amended by PL 98-371 in 1984
Amended by PL 98-616 in 1984, The Hazardous and Solid Waste Amendment
Amended by PL 99-339 in 1986
Amended by PL 99-499 in 1986
Amended by PL 100-582 in 1988.

Responsible Federal Agencies. The following federal agency and committee have the primary responsibilities for implementing the Act:

Environmental Protection Agency. Under Subtitle B, Section 2001 of RCRA, the Office of Solid Waste was established within the EPA to monitor the implementation of the Act.

Interagency Coordinating Committee. Under Section 2001 of RCRA, an Interagency Coordinating Committee was established and made responsible for coordinating all activities dealing with resource conservation and recovery from solid waste carried out by the EPA, the Department of Energy, the Department of Commerce, and all other federal agencies that conduct such activities pursuant to this or another act.

References

1. Public Law 94-580.
2. CFR Title 40, Parts 240 et. seq.
3. CFR Title 40, Parts 100 et. seq.
4. Environment Reporter, Federal Laws, Vol. 2, 1989.
5. Federal Register, Vol. 54, No. 169:36596, 1989.

Title III: Standards and Enforcement

Under this title, the effluent limitations for point sources, other than publicly owned treatment works, require the application of the best applicable control technology currently available.

Section 301: Effluent Limitations
Section 302: Water Quality Related Effluent Limitations
Section 303: Water Quality Standards and Implementation Plans
Section 306: National Standards of Performance
Section 307: Toxic and Pretreatment Effluent Standards
Section 308: Inspections, Monitoring, and Entry
Section 314: Clean Lakes.

Title IV: Permits and Licenses

Section 402: National Pollutant Discharge Eliminations System (NPDES)
Section 404: Permit for Dredged or Fill Material.

Regulations. Certain regulations for implementing the CWA are promulgated and administered by the EPA. The most pertinent regulations set forth deal with 1) water quality planning, management, and standards, 2) hazardous waste designation, 3) the NPDES permit program, and 4) state program requirements. These regulations are published under 40 CFR, Subchapter D. CFR Chapter 40 contains regulations for general provisions for effluent guidelines and standards (40 CFR 401) and pretreatment standards (40 CFR 403).

Legislative History. The CWA has been amended to include new and/or changed authority. In addition, some amendments use the CWA as a vehicle to establish other federal statutes (acts); i.e., the Indian Reorganization Act. In any event, each amendment may have applicability to the siting of an oil shale plant.

The legislative history of CWA is:

Enacted by PL 92-500 in 1972, Federal Water Pollution Control Act
Amended by PL 93-207 in 1973
Amended by PL 93-243 in 1974
Amended by PL 93-592 in 1975
Amended by PL 94-238 in 1976
Amended by PL 94-273 in 1976, Fiscal Year Adjustment Act
Amended by PL 94-558 in 1976
Amended by PL 95-217 in 1977, Clean Water Act
Amended by PL 95-576 in 1978
Amended by PL 96-148 in 1979
Amended by PL 96-478 in 1980
Amended by PL 96-483 in 1980
Amended by PL 96-510 in 1980
Amended by PL 96-561 in 1980
Amended by PL 97-35 in 1981
Amended by PL 97-117 in 1981
Amended by PL 97-164 in 1982
Amended by PL 97-440 in 1983
Amended by PL 100-4 in 1987, Water Quality Act

to oil shale facilities could possibly include spent catalysts and processed shale.

Industries that generate, transport, treat, store, or dispose of waste removed from temporary exclusion by 40 CFR, Part 261, Subpart C, will be required to notify either EPA or an authorized state of these activities pursuant to Section 3010 of RCRA.

Legislative History. The RCRA has been amended to include new and/or changed authority. In addition, some amendments use the RCRA as a vehicle to establish other federal statutes (acts); i.e., the Solid Waste Disposal Act. In any event, each amendment should be studied to determine its impact on the siting of an oil shale plant.

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Amended by PL 96-510 in 1980, Comprehensive Environmental Response, Compensation, and Liability Act
Amended by PL 97-272 in 1982
Amended by PL 97-375 in 1982, Congressional Reports Elimination Act
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References

1. Public Law 94-580.
2. CFR Title 40, Parts 240 et. seq.
3. CFR Title 40, Parts 100 et. seq.
4. Environment Reporter, Federal Laws, Vol. 2, 1989.
5. Federal Register, Vol. 54, No. 169:36596, 1989.

Act as a vehicle to establish other federal statutes. In any event, each amendment should be studied to determine if there would be an impact on a particular site location of an oil shale plant. The legislative history of the Endangered Species Act is as follows:

Enacted by PL 93-205 in 1973, Endangered Species Act
Amended by PL 94-325 in 1976
Amended by PL 94-359 in 1976
Amended by PL 95-212 in 1977
Amended by PL 95-632 in 1978
Amended by PL 96-159 in 1979
Amended by PL 96-246 in 1980
Amended by PL 97-79 in 1981
Amended by PL 97-304 in 1982
Amended by PL 98-327 in 1984
Amended by PL 99-659 in 1986
Amended by PL 100-478 in 1988
Amended by PL 100-653 in 1988
Amended by PL 100-707 in 1988.

Responsible Federal Agency. The following federal agency has the primary responsibility to implement the act:

Department of the Interior. The act empowers the Department of the Interior to determine and identify endangered species. The department has the responsibility to regulate and take necessary action to conserve such species. The Office of Endangered Species, which is within the U.S. Fish and Wildlife Service, implements promulgations and enforcement activities as provided under the act.

References

1. Public Law 93-205.
2. Federal Laws and Treaties of Interest to the U.S. Fish and Wildlife Service, Compiled by the Office of Legislative Services, U.S. Fish and Wildlife Service, Department of the Interior, 1989.
3. CFR Title 40, Part 6.
4. Environment Reporter, Federal Laws, Vol. 2, 1989.

Toxic Substances Control Act of 1976

Law. The purpose of the Toxic Substances Control Act (TSCA) prevents the increasing build-up of cancer-causing, birth defect-causing, and genetic-damaging substances both in the atmosphere and in the environment. Sections of the Act that could apply to oil shale producers, in the event that spent shale is determined to be toxic, are:

Title I:

Section 115: In Place Toxic Pollutant

Title III:

Section 307: Toxic and Pretreatment Effluent Standards.

Amended by PL 100-202 in 1987
Amended by PL 100-581 in 1988, Indian Reorganization Act
Amended by PL 100-653 in 1988, Lacey Act
Amended by PL 100-688 in 1988, Ocean Dumping of Sewage Sludge and Industrial Waste.

Responsible Federal Agencies. The following federal agencies have primary responsibilities for implementing the act:

Environmental Protection Agency. Public Law 100-4 amended Title I, Section 101 of the CWA to empower the EPA to implement and monitor the intent of the act. The CEQ is also charged with the responsibility to implement the act. Title VI, Section 402 indicates that EPA may, after opportunity for public hearing, issue a permit for discharge of any pollutant or combination of pollutants that have discharge conditions applicable to the requirements under Sections 301, 302, 306, 307, 308, and 403 of this act.

U.S. Army Corps of Engineers. Title VI, Section 404 empowers the U.S. Army Corps of Engineers to establish regulations in controlling the discharge of materials in navigable waters.

References

1. Public Law 92-500.
2. CFR Title 40, Subchapter D, Parts 104 et. seq.
3. Environment Reporter, Federal Laws, Vol. 2, 1989.

Secondary Laws and Regulations

Endangered Species Act of 1973

Law. The purpose of the Endangered Species Act is to protect various endangered or threatened species. The act protects various species of fish, wildlife, and plants, which have been rendered extinct as a result of natural disasters and the consequences of economic growth and development untempered by adequate concern and conservation. The following sections of the Endangered Species Act could have a direct impact on the siting of an oil shale plant:

Section 4: Determination of Endangered Species and Threatened Species
Section 6: Cooperation with States
Section 7: Interagency Cooperation.

Regulations. The specific location of each endangered species is not determined; however, the list of each endangered species is published. The following regulations under the act could be applicable to the siting of an oil shale plant:

40 CFR 6: EPA Regulations on Implementation of NEPA Procedures

Endangered Plant and Wildlife List.

Legislative History. The Act has been amended to include new and/or changed authority. In addition, some amendments use the Endangered Species

References

1. Toxic Substances Control Act, (P.L. 94-469), 94 Congress, S. 3149, 1976.
2. Federal Laws and Treaties of Interest to the U.S. Fish and Wildlife Service, Compiled by the Office of Legislative Services, U.S. Fish and Wildlife Service, Department of the Interior, 1989.
3. The Layman's Guide to the Toxic Substances Control Act, EPA, 1987.
4. Toxic Substances Control Act: A Guide for Chemical Importer and Exporter, Volume 1, EPA.
5. Summary of Regulations, Published Under the Toxic Substances Control Act, The Environmental Assistance Division, EPA, 1989.
6. CFR Title 40, Parts 700 et. seq.
7. CFR Title 40, Parts 100 et. seq.
8. CFR Title 40, Parts 400 et. seq.
9. Synfuels Week, October 11, 1982.
10. Environment Reporter, Federal Law, Vol. 2, 1989.

Rivers and Harbors Act of 1899

Law. The primary purpose of this act is to maintain adequate control on dredge and fill operations carried out in navigable waters. The following sections of the act have an indirect implication on siting of an oil shale plant:

Section 407: Deposit of Refuse in Navigable Waters Generally
Section 407(a): Deposit of Debris of Mines and Stamp Works.

Regulations. The following regulations have an indirect implication on the Rivers and Harbors Act and may effect the siting of an oil shale plant:

33 CFR 209: Army Corps of Engineers Regulations on Navigable Waters
40 CFR 6: EPA Regulations on Implementation of National Environmental Policy Act Procedures
40 CFR 230: EPA Interim Regulations on Discharge of Dredge or Fill Material into Navigable Waters
40 CFR 232: EPA Rules on Activities Exempt from Dredge and Fill (404) Permit Requirements
40 CFR 233: EPA Regulations on State Dredge or Fill (404) Permit Program Requirements.

In Section 404 of the CWA, states have the authority to provide permits for dredge and fill operations on non-navigable waters. Permits under Section 404 could also be subject to the NEPA and the development of an EIS.

Legislative History. The Rivers and Harbors Act was enacted in 1899 as the Refuse Act. The act is now listed as 33 USC 30, Stat. 1151.

Responsible Federal Agencies. The following federal agencies are charged with the primary responsibilities for implementing and monitoring the objectives set forth by the Rivers and Harbors Act:

U.S. Army Corps of Engineers. Under Section 10 of the Act (33 USC 403,; 30 Stat. 1151), the Corps of Engineers is charged with the responsibility to regulate and license any construction activity operated on a navigable

Amended by PL 100-202 in 1987

Amended by PL 100-581 in 1988, Indian Reorganization Act

Amended by PL 100-653 in 1988, Lacey Act

Amended by PL 100-688 in 1988, Ocean Dumping of Sewage Sludge and Industrial Waste.

Responsible Federal Agencies. The following federal agencies have primary responsibilities for implementing the act:

Environmental Protection Agency. Public Law 100-4 amended Title I, Section 101 of the CWA to empower the EPA to implement and monitor the intent of the act. The CWA is also charged with the responsibility to implement the act. Title VI, Section 402 indicates that EPA may, after opportunity for public hearing, issue a permit for discharge of any pollutant or combination of pollutants that have discharge conditions applicable to the requirements under Sections 301, 302, 306, 307, 308, and 403 of this act.

U.S. Army Corps of Engineers. Title VI, Section 404 empowers the U.S. Army Corps of Engineers to establish regulations in controlling the discharge of materials in navigable waters.

References

1. Public Law 92-500.
2. CFR Title 40, Subchapter D, Parts 104 et. seq.
3. Environment Reporter, Federal Laws, Vol. 2, 1989.

Secondary Laws and Regulations

Endangered Species Act of 1973

Law. The purpose of the Endangered Species Act is to protect various endangered or threatened species. The act protects various species of fish, wildlife, and plants, which have been rendered extinct as a result of natural disasters and the consequences of economic growth and development untempered by adequate concern and conservation. The following sections of the Endangered Species Act could have a direct impact on the siting of an oil shale plant:

Section 4: Determination of Endangered Species and Threatened Species

Section 6: Cooperation with States

Section 7: Interagency Cooperation.

Regulations. The specific location of each endangered species is not determined; however, the list of each endangered species is published. The following regulations under the act could be applicable to the siting of an oil shale plant:

40 CFR 6: EPA Regulations on Implementation of NEPA Procedures

Endangered Plant and Wildlife List.

Legislative History. The Act has been amended to include new and/or changed authority. In addition, some amendments use the Endangered Species

Section 1426: Regulation of State Programs
Section 1427: Sole Source Aquifer Demonstration Program
Section 1428: State Programs to Establish Wellhead Protection Area.

Part D: Emergency Power

Section 1431: Emergency Power

Part E: General Provisions

Section 1441: Assurance of Availability of Adequate Supplies of
Chemicals Necessary for Treatment of Water
Section 1445: Records and Inspection
Section 1446: National Drinking Water Advisory Council
Section 1451: Indian Tribes
40 CFR 141: EPA National Primary Drinking Water Regulations
40 CFR 142: EPA National Drinking Water Implementation Regulations
40 CFR 143: EPA National Secondary Drinking Water Regulations
40 CFR 144: Permit Regulations for the Underground Injection Control
Program
40 CFR 145: Regulations on State Underground Injection Control Program
Requirements
40 CFR 146: Criteria and Standards for Underground Injection Control
Program
40 CFR 147: EPA Regulations on State Underground Injection Control
Program
40 CFR 148: Regulations on Hazardous Waste Disposal Restriction for
Class I Wells
40 CFR 149: Regulations on Review of Projects Affecting Sole Source
Aquifer.

The underground injection code (UIC) is a critical aspect of the SDWA for synthetic fuels operations. The UIC is designed to prevent underground injection, which endangers underground drinking water sources.

Legislative History. The SDWA has been amended to include new and/or changed authority. In addition, some amendments use the SDWA as a vehicle to establish other federal statutes. In any event, each amendment should be studied to determine its impact on the siting of an oil shale plant. The legislative history of the SDWA is as follows:

Enacted PL 93-523 in 1974, Safe Drinking Water Act
Amended PL 94-317 in 1976
Amended PL 94-484 in 1976
Amended PL 95-190 in 1977
Amended PL 96-63 in 1979
Amended PL 96-502 in 1980
Amended PL 98-620 in 1984
Amended PL 99-339 in 1986.

Responsible Federal Agencies. The following federal agencies are charged with the primary responsibilities for implementing and monitoring the intent of the SDWA:

waterway. Various permits for construction of piers, jetties, or similar structures, dredge or and fill, and discharge of refuse in navigable waters could be granted by the Corps of Engineers but would have to be obtained from the U.S. Fish and Wildlife Service and Environmental Protection Agency (EPA).

Environmental Protection Agency. The EPA is also empowered by the Rivers and Harbors Act to question the proposed applications before any water operation can be fully operational.

U.S. Fish and Wildlife Service. The Fish and Wildlife Service, like EPA, is empowered by the Rivers and Harbors Act to question proposed applications and proposed plant sittings before any operation can be fully operational.

References

1. Public Law 33 USC 30, Stat. 1151.
2. Federal Laws and Treaties of Interest to the U.S. Fish and Wildlife Service, Compiled by the Office of Legislative Services, U.S. Fish and Wildlife Service, Department of the Interior, 1989.
3. Communication with Mr. John Davidson, Office of Policy, Planning, and Evaluation, U.S. EPA, Washington, D.C. 20460, April 22, 1990.
4. Communication with Mr. Daniel J. Fiorino, Associate Director, Office of Policy, Planning, and Evaluation, U. S. EPA, Washington, D.C. 20460, April 22, 1990.
5. CFR Title 33, Part 209.
6. CFR Title 40, Part 6.
7. CFR Title 40, Parts 230-233.
8. Environment Reporter, Federal Law, Vol. 2, 1989.

Safe Drinking Water Act of 1974

Law. The purpose of the Safe Drinking Water Act (SDWA) is to secure and maintain the quality of drinking water and to protect it from contamination in public water systems as well as surface and underground sources.

Regulations. The following regulations are parts of the SDWA and may have an impact on siting an oil shale plant:

Part B: Public Water Systems

Section 1412: National Drinking Water Regulations
Section 1413: State Primary Enforcement Responsibility
Section 1414: Enforcement of Drinking Water Regulations
Section 1415: Variances
Section 1416: Exemptions.

Part C: Protection of Underground Sources of Drinking Water

Section 1421: Regulations for State Programs
Section 1422: State Primary Enforcement Responsibility
Section 1423: Failure of State To Assure Enforcement of Program
Section 1424: Interim Regulations of Underground Injection
Section 1425: Optional Demonstration by States Relating to Oil or Natural Gas

Legislative History. The Wild and Scenic Rivers Act has been amended to include new and/or changed authority. In addition, some amendments use the Wild and Scenic Rivers Act as vehicle to establish other federal statutes. In any event, each amendment should be studied to determine its impact on the siting of an oil shale plant. The legislative history of the Wild and Scenic Rivers Act is as follows:

Enacted by PL 90-542 in 1968, Wild and Scenic Rivers Act

Amended by PL 92-560 in 1972

Amended by PL 93-279 in 1974

Amended by PL 93-621 in 1975

Amended by PL 94-199 in 1975

Amended by PL 94-273 in 1976

Amended by PL 94-407 in 1976

Amended by PL 94-486 in 1976

Affected by PL 95-91 in 1977

Amended by PL 95-625 in 1978

Amended by PL 96-87 in 1979

Amended by PL 96-199 in 1980

Amended by PL 96-312 in 1980

Amended by PL 96-344 in 1980

Amended by PL 96-487 in 1980

Amended by PL 96-580 in 1980

Affected by PL 98-231 in 1984

Amended by PL 98-323 in 1984

Amended by PL 98-406 in 1984

Amended by PL 98-496 in 1984

Amended by PL 99-530 in 1986

Amended by PL 99-590 in 1986

Amended by PL 99-663 in 1986

Amended by PL 100-33 in 1987

Amended by PL 100-149 in 1987

Amended by PL 100-150 in 1987

Amended by PL 100-174 in 1987

Amended by PL 100-534 in 1988

Amended by PL 100-547 in 1988

Amended by PL 100-554 in 1988

Amended by PL 100-557 in 1988

Amended by PL 100-633 in 1988.

Responsible Federal Agency. The following federal agency has the primary responsibility to implement the Wild and Scenic Rivers Act:

Department of the Interior. Section 6 of the act empowers the Department of the Interior to oversee and implement the intent of the act. If mining activities come in conflict with a given locality, prohibition of the activity may result. The act provides authority to the Department of the Interior to set criteria for determining suitability and establishes restrictions on activities that can be undertaken on a designated area. Specific wilderness areas, acreages, and establishing legislation are listed in the "Annual Review of Lands Administered by the Fish and Wildlife Service for Potential Wilderness Area."

waterway. Various permits for construction of piers, jetties, or similar structures, dredge or and fill, and discharge of refuse in navigable waters could be granted by the Corps of Engineers but would have to be obtained from the U.S. Fish and Wildlife Service and Environmental Protection Agency (EPA).

Environmental Protection Agency. The EPA is also empowered by the Rivers and Harbors Act to question the proposed applications before any water operation can be fully operational.

U.S. Fish and Wildlife Service. The Fish and Wildlife Service, like EPA, is empowered by the Rivers and Harbors Act to question proposed applications and proposed plant sittings before any operation can be fully operational.

References

1. Public Law 33 USC 30, Stat. 1151.
2. Federal Laws and Treaties of Interest to the U.S. Fish and Wildlife Service, Compiled by the Office of Legislative Services, U.S. Fish and Wildlife Service, Department of the Interior, 1989.
3. Communication with Mr. John Davidson, Office of Policy, Planning, and Evaluation, U.S. EPA, Washington, D.C. 20460, April 22, 1990.
4. Communication with Mr. Daniel J. Fiorino, Associate Director, Office of Policy, Planning, and Evaluation, U. S. EPA, Washington, D.C. 20460, April 22, 1990.
5. CFR Title 33, Part 209.
6. CFR Title 40, Part 6.
7. CFR Title 40, Parts 230-233.
8. Environment Reporter, Federal Law, Vol. 2, 1989.

Safe Drinking Water Act of 1974

Law. The purpose of the Safe Drinking Water Act (SDWA) is to secure and maintain the quality of drinking water and to protect it from contamination in public water systems as well as surface and underground sources.

Regulations. The following regulations are parts of the SDWA and may have an impact on siting an oil shale plant:

Part B: Public Water Systems

Section 1412: National Drinking Water Regulations
Section 1413: State Primary Enforcement Responsibility
Section 1414: Enforcement of Drinking Water Regulations
Section 1415: Variances
Section 1416: Exemptions.

Part C: Protection of Underground Sources of Drinking Water

Section 1421: Regulations for State Programs
Section 1422: State Primary Enforcement Responsibility
Section 1423: Failure of State To Assure Enforcement of Program
Section 1424: Interim Regulations of Underground Injection
Section 1425: Optional Demonstration by States Relating to Oil or Natural Gas

Regulations

There are no particular rules and regulations that are directly related to this act pertaining to the siting of an oil shale processing plant in Alabama.

Legislative History

The legislative history of the AEMA is as follows:

Enacted by Acts of 1982, No. 612

Amended by Acts of 1983, No. 131, 84-783, 85-755, 86-472, 86-542, 88-537.

Responsible State Agency

The following state agency has the primary responsibility to promulgate and monitor the intent of this act:

Department of Environmental Management. Under Section 4 of the AEMA, the Alabama Department of Environmental Management (ADEM) was established. The ADEM is charged with the responsibility, according to Section 5 of the act, to promulgate rules, regulations, and standards set forth by the environmental laws in order to carry out the provision and intent of the act. The department is also empowered to develop environmental policy to carry out the environmental laws of the federal government.

References

1. Environment Reporter, State Air Laws, Vol. 1, 1989.
2. Communication with Ms. Elizabeth Price, Secretary, Legal Division, Surface Mining Commission, Alabama Department of Environmental Management, July 1989 -- June 1990.
3. Communication with Ms. Marilyn Elliott, Permit and Services Division, Alabama Department of Environmental Management, August 1989 -- May 1990.

Alabama Water Pollution Control Act

Law

The Alabama Water Pollution Control Act (AWPCA) declares that it is a state policy to 1) conserve the waters of the state, 2) protect, maintain, and improve the quality for public water supplies, and 3) provide for the prevention, abatement, and control of new and existing water pollution.

Regulations

According to the rules and regulations of the ADEM, Division 6 of the Water Quality Program, the following chapters of rules and regulations may have a direct impact in siting an oil shale plant:

Chapter 5: Alabama Water Quality Program Regulations:

References

1. Public Law 90-542.
2. Federal Laws and Treaties of Interest to the U.S. Fish and Wildlife Service, Compiled by the Office of Legislative Services, U.S. Fish and Wildlife Service, Department of the Interior, 1989.
3. CFR Title 40, Part 6.
4. CFR Title 40, Part 130.
5. Environment Reporter, Federal Laws, Vol. 2, 1989.

ADDRESSES OF RESPONSIBLE FEDERAL AGENCIES:

RIVERS AND HARBORS ACT
SAFE DRINKING WATER ACT
TOXIC SUBSTANCES CONTROL ACT

United States Environmental Protection Agency
Office of Policy, Planning, and Evaluation
Washington, D.C. 20640
Contact: Mr. Daniel J. Fiorino, Associate Director
Phone:

Contact: Mr. John Davidson
Phone:

TSCA Assistance Office (TS-799)
Office of Toxic Substances
U.S. Environmental Protection Agency, Room E-543
401 M Street, S.W.
Washington, D.C. 20460
Contact: Mr. Edward Klein, Director
Phone: (202) 554-1404

TSCA Section 8(e) (TS 778)
Office of Toxic Substances
U.S. Environmental Protection Agency, Room E-543
401 M Street, S.W.
Washington, D.C. 20460
Contact: Mr. David R. Williams, Coordinator
Phone: (202) 382-3468

State Laws and Regulations

Alabama

Alabama Environmental Management Act

Law

The purpose of the Alabama Environmental Management Act (AEMA) is to develop a comprehensive and coordinated program of environmental management in order to improve the ability of the state to respond to environmental problems more efficiently. It is the intent of this act to establish the Alabama Department of Environmental Management (ADEM) within the executive branch of the state government.

Alabama Air Pollution Control Act of 1971

Law

The Alabama Air Pollution Control Act of 1971 declares that it is the public policy to achieve and maintain such levels of air quality as will protect human health and safety. It is the intent of this act to provide for a coordinated statewide program of air pollution prevention, abatement, and control in order to secure and maintain the appropriate levels of air quality.

Regulations

According to the Alabama Administrative Code, Division 3 of the ADEM, the following air pollution control regulations could have an impact on siting an oil shale plant.

Alabama Air Pollution Control Regulations

Chapter 1: General Provision

Section .03: Ambient Air Quality Standards
Section .08: Prohibition of Air Pollution
Section .09: Variances

Chapter 2: Air Pollution Emergency

Section .02: Episode Criteria
Section .03: Special Episode Criteria
Section .04: Emission Reduction Plans
Section .05: Two Contaminant Episodes
Section .06: General Episodes

Chapter 4: Control of Particulate Emissions

Section .01: Visible Emission
Section .02: Fugitive Dust and Fugitive Emission
Section .04: Process Industries-General

Chapter 5: Control of Sulfur Compound Emissions

Section .01: Fuel Combustion
Section .03: Petroleum Production
Section .05: Process Industries-General

Chapter 6: Control of Organic Emissions

Section .04: Fixed-Roof Petroleum Liquid Storage Vessels
Section .08: Petroleum Refinery Sources
Section .21: Leaks from Petroleum Refinery Equipments
Section .31: Petroleum Refinery Source
Section .42: Leaks from Petroleum Refinery Equipment
Section .47: Leaks from Coke Byproduct Recovery Plant Equipment

References

1. Public Law 90-542.
2. Federal Laws and Treaties of Interest to the U.S. Fish and Wildlife Service, Compiled by the Office of Legislative Services, U.S. Fish and Wildlife Service, Department of the Interior, 1989.
3. CFR Title 40, Part 6.
4. CFR Title 40, Part 130.
5. Environment Reporter, Federal Laws, Vol. 2, 1989.

ADDRESSES OF RESPONSIBLE FEDERAL AGENCIES:

RIVERS AND HARBORS ACT
SAFE DRINKING WATER ACT
TOXIC SUBSTANCES CONTROL ACT

United States Environmental Protection Agency
Office of Policy, Planning, and Evaluation
Washington, D.C. 20640
Contact: Mr. Daniel J. Fiorino, Associate Director
Phone:

Contact: Mr. John Davidson
Phone:

TSCA Assistance Office (TS-799)
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401 M Street, S.W.
Washington, D.C. 20460
Contact: Mr. David R. Williams, Coordinator
Phone: (202) 382-3468

State Laws and Regulations

Alabama

Alabama Environmental Management Act

Law

The purpose of the Alabama Environmental Management Act (AEMA) is to develop a comprehensive and coordinated program of environmental management in order to improve the ability of the state to respond to environmental problems more efficiently. It is the intent of this act to establish the Alabama Department of Environmental Management (ADEM) within the executive branch of the state government.

Alabama Hazardous Waste Management and Minimization Act

Law

The purpose of the Alabama Hazardous Waste Management and Minimization Act is to seek and retain authorization to operate the state hazardous waste management program. It is also the intent of this act to encourage the minimization of hazardous waste generation, transportation, and land disposal and to achieve consistency with the federal hazardous waste management program, rules, regulations, guidelines, and criteria. Under the authority of this chapter of Alabama law, certain hazardous waste management technologies or the application of certain hazardous management technologies to specific wastes may be limited or banned.

Regulations

The following regulations may have a direct impact on siting an oil shale processing plant:

Alabama Hazardous Waste Management Regulations

Chapter 14-2: Identification and Listing of Hazardous Waste

Section .02: Criteria or Identifying the Characteristic of Hazardous Waste and for Listing Hazardous Waste

Section .03: Characteristic of Hazardous Waste

Section .04: List of Hazardous Waste

Chapter 14-3: Standards Applicable to Generators of Hazardous Waste

Section .03: Pre-Treatment Requirement

Chapter 14-4: Standards Applicable to Transporters of Hazardous Waste

Section .03: Hazardous Waste Discharge

Chapter 14-5: Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities

Section .02: General Facility Standards

Section .11: Surface Impoundment

Section .12: Waste Piles

Section .13: Land Treatment

Chapter 14-8: Permit Programs

Chapter 14-9: Land Disposal Restriction

Legislative History

The legislative history of the Alabama Hazardous Wastes Management and Minimization Act is as follows:

Enacted by Alabama Acts of 1978, No. 129

Chapter 7: Carbon Monoxide Emission

Section .02: Petroleum Process

Chapter 8: Nitrogen Oxide Emission

Chapter 10: Standards of Performance for New Stationary Sources

Chapter 11: National Emission Standards for Hazardous Air Pollutants

Chapter 14: Permits

Legislative History

The legislative history of the Alabama Air Pollution Control Act of 1971 is as follows:

Enacted by Acts of 1971, No. 769
Amended by Acts of 1980, No. 439
Amended by Acts of 1986, No. 542.

Responsible State Agencies

The following state agencies have the primary responsibilities to implement and monitor the intent of the Alabama Air Pollution Control Act:

Environmental Management Commission or Air Pollution Control Agency.

Under Section 10 of the Alabama Air Pollution Control Act of 1971, the Environmental Management Commission, which is also designated as the Air Pollution Control Agency, is authorized to prepare and develop a comprehensive plan for the prevention, abatement, and control of air pollution in the state. The commission is authorized to advise, consult, contract, and cooperate with other agencies of the state, local government, industries, federal government, and interest groups in order to carry out the purposes of the Federal Clean Air Act, as amended.

Department of Environmental Management. The ADEM was created under Section 22-22A-4 of the AEMA. The Air Pollution Control Agency was established within the structure of the Alabama Department of Environmental Management. In general, the department is empowered to promulgate and revise appropriate criteria, standards, rules, and regulations pertaining to air pollution activities in the state of Alabama.

References

1. Air Pollution Control Program, Administrative Code, Alabama Department of Environmental Management, Division 3, June 1989.
2. Environment Reporter, State Air Laws, Vol. 1, 1989.
3. Communication with Ms. Elizabeth Price, Secretary, Legal Division, Surface Mining Commission; Alabama Department of Environmental Management, July 1989 -- June 1990.
4. Communication with Ms. Marilyn Elliott, Permit and Services Division, Alabama Department of Environmental Management, August 1989 -- June 1990.

Alabama Solid Waste Management Regulations

Chapter 13-2: Storage, Collection, and Transportation

Chapter 13-3: Processing and Recycling

Chapter 13-4: Permit Requirements

Section .01: Solid Waste Disposal Site
Section .13: Site Geology and Hydrology
Section .14: Groundwater Resources
Section .16: Explosive Gases
Section .17: Drainage
Section .21: General Operational Standards for Disposal.

Legislative History

The legislative history of the Alabama Solid Waste Act is as follows:

Enacted by Alabama Acts of 1969, No. 771
Amended by Alabama Acts of 1971, No. 1197, 2247, 82-612, No. 86-542,
88-655.

Responsible State Agency

The following state agency has the primary responsibility to implement and monitor the objectives of this act:

Department of Environmental Management. The ADEM was created under Section 22-22A-4 of the AEMA. The department has exclusive regulatory authority over all solid waste generation, storage, transportation, treatment, disposal, and other management practices in the state. The department is empowered to promulgate and revise appropriate criteria, rules, and regulations pertaining to identification, storage, disposal, and pretreatment of solid waste.

References

1. Environment Reporter, Solid Waste and Land Use, Vol. 1, 1989.
2. Communication with Ms. Elizabeth Price, Secretary, Legal Division, Surface Mining Commission, Alabama Department of Environmental Management, May 25, 1990.
3. Communication with Ms. Marilyn Elliott, Permit and Services Division, Alabama Department of Environmental Management, May 25, 1990.

Alabama Surface Mining Control and Reclamation Act

Law

The objective of the Alabama Surface Mining Control and Reclamation Act is to provide for the safe, responsible, and reasonable reclamation of lands upon which surface disturbances have been created by surface mining and surface effects of underground mining. A statewide program was established to

Chapter 7: Carbon Monoxide Emission

Section .02: Petroleum Process

Chapter 8: Nitrogen Oxide Emission

Chapter 10: Standards of Performance for New Stationary Sources

Chapter 11: National Emission Standards for Hazardous Air Pollutants

Chapter 14: Permits

Legislative History

The legislative history of the Alabama Air Pollution Control Act of 1971 is as follows:

Enacted by Acts of 1971, No. 769
Amended by Acts of 1980, No. 439
Amended by Acts of 1986, No. 542.

Responsible State Agencies

The following state agencies have the primary responsibilities to implement and monitor the intent of the Alabama Air Pollution Control Act:

Environmental Management Commission or Air Pollution Control Agency.
Under Section 10 of the Alabama Air Pollution Control Act of 1971, the Environmental Management Commission, which is also designated as the Air Pollution Control Agency, is authorized to prepare and develop a comprehensive plan for the prevention, abatement, and control of air pollution in the state. The commission is authorized to advise, consult, contract, and cooperate with other agencies of the state, local government, industries, federal government, and interest groups in order to carry out the purposes of the Federal Clean Air Act, as amended.

Department of Environmental Management. The ADEM was created under Section 22-22A-4 of the AEMA. The Air Pollution Control Agency was established within the structure of the Alabama Department of Environmental Management. In general, the department is empowered to promulgate and revise appropriate criteria, standards, rules, and regulations pertaining to air pollution activities in the state of Alabama.

References

1. Air Pollution Control Program, Administrative Code, Alabama Department of Environmental Management, Division 3, June 1989.
2. Environment Reporter, State Air Laws, Vol. 1, 1989.
3. Communication with Ms. Elizabeth Price, Secretary, Legal Division, Surface Mining Commission, Alabama Department of Environmental Management, July 1989 -- June 1990.
4. Communication with Ms. Marilyn Elliott, Permit and Services Division, Alabama Department of Environmental Management, August 1989 -- June 1990.

Section K: Special Performance Standards -- In Situ Processing.

Legislative History

The legislative history of the Alabama Surface Mining Control and Reclamation Act is as follows:

Enacted by Acts of 1981, No. 81-435

Amended by Acts of 1983, No. 83-774

Amended by Acts of 1986, No. 86-106.

Responsible State Agency

The following state agency has the primary responsibility to implement and monitor the Alabama Surface Mining Control and Reclamation Act:

Alabama Surface Mining Commission. Under Chapter 16, Section 73, of the Alabama Surface Mining Control and Reclamation Act, the Alabama Surface Mining Commission was established. The commission is charged with the responsibilities to monitor and oversee the intent of the act. Section 74 of the act empowers the commission to issue orders, promulgate, and enforce rules, regulations, and standards set forth by the act and the Office of Surface Mining Reclamation and Enforcement of the U.S. Department of the Interior. Under Section 880-X-2A-.05 of the Alabama Surface Mining Rules, the commission has the responsibility for the regulation of and issuing permits for coal exploration and surface mining and reclamation operation.

References

1. **The Alabama Surface Mining Control and Reclamation Act, 1981.**
2. **State of Alabama Surface Mining Commission, Amended Rules and Regulations, Adopted 1983-1984.**
3. **Environment Reporter, State Law, Mining, Vol. 1, 1989.**
4. **Communication with Ms. Elizabeth Price, Secretary, Legal Division, Surface Mining Commission, Alabama Department of Environmental Management, May 25, 1990.**
5. **Communication with Ms. Marilyn Elliott, Permit and Services Division, Alabama Department of Environmental Management, May 25, 1990.**

ADDRESSES OF THE STATE AGENCIES

State Unit

ALABAMA ENVIRONMENTAL MANAGEMENT ACT
ALABAMA WATER POLLUTION CONTROL ACT
ALABAMA AIR POLLUTION CONTROL ACT OF 1971
ALABAMA SOLID WASTES DISPOSAL ACT
ALABAMA HAZARDOUS WASTES MANAGEMENT AND MINIMIZATION ACT

Alabama Department of Environmental Management
Permit and Services Division
1751 Cong. W. L. Dickinson Drive

reduce adverse effects to the environment resulting from surface coal mining operations. It is also the intent of this act to assure that surface coal mining activities are not conducted where reclamation, as required by this law, is not feasible.

Regulations

The following rules and regulations set forth by different Alabama state agencies may have a significant impact to the siting of an oil shale plant:

Department of Conservation and Natural Resources:

Alabama Abandoned Mine Reclamation Act

Department of Environmental Management of Surface Mining Regulations
(Division 6 of Water Quality Program):

Alabama Mine Drainage Regulations

Section 6-9-.03: Pollutant Abatement and/or Prevention Plan

Guidelines for Minimizing The Effects on Surface Mining and Surface
Effects of Underground Mining on Water Quality Surface Mining Commission
Rules and Regulations:

Alabama Surface Mining and Reclamation Rules

Chapter 880-X-7: Areas Unsuitable for Mining

Section A: General

Section B: Areas Designated by the Act

Section C: Criteria for Designating Areas as Unsuitable for Surface
Coal Mining Operations

Section D: State Processes for Designating Areas Unsuitable for
Surface Coal Mining Operations

Chapter 880-X-10: Performance Standards

Section A: Performance Standards -- General

Section B: Performance Standards -- Coal Exploration

Section C: Performance Standards -- Surface Mining Activities

Section D: Performance Standards -- Underground Mining Activities

Section E: Special Performance Standards -- Concurrent Surface and
Underground Mining

Section J: Special Performance Standards -- Coal Processing Plants
and Support Facilities Located at or Near the Mine Site
but not Within the Permit Area of Mine

Jasper, Alabama 35502-2390
Contact: Ms. Elizabeth A. Price, Secretary
Phone: (205) 221-4130

Indiana

Indiana Environmental Management Act

Law

The purpose of this article is to 1) provide for evolving policies for comprehensive environmental development and control on a statewide basis, 2) unify, coordinate, and implement programs to provide for the most beneficial use of the resources of the state, and 3) protect and enhance the quality of the environment of the state.

Regulations

There are no direct rules and regulations that are specifically outlined in this act that may have a direct or indirect impact on the siting of an oil shale processing plant in the state of Indiana.

Legislative History

The legislative history of the Indiana Environmental Management Act (IEMA) is as follows:

Enacted by Indiana Acts of 1972, PL 100
Amended by Indiana Acts of 1973, PL 126
Amended by Indiana Acts of 1974, PL 50
Amended by Indiana Acts of 1978, PL 2
Amended by Indiana Acts of 1979, PL 17, 40
Amended by Indiana Acts of 1980, PL 103
Amended by Indiana Acts of 1981, PL 11, 33, 95
Amended by Indiana Acts of 1982, PL 107, 108, 127
Amended by Indiana Acts of 1983, PL 171, 311
Amended by Indiana Acts of 1984, PL 17
Amended by Indiana Acts of 1985, PL 143, 152
Amended by Indiana Acts of 1986, PL 112, 118
Amended by Indiana Acts of 1987, PL 6, 7, 34, 38, 160, 161, PL 168, PL 169, 170
Amended by Indiana Acts of 1988, PL 69, 109, 111
Amended by Indiana Acts of 1989, PL 163.

Responsible State Agency

The following state agency has the primary responsibility to monitor and implement the intent of this act:

Department of Environmental Management. Chapter 2 of the IEMA created the Department of Environmental Management (DEM) within the executive branch of the state government. The department consists of the Office of Environmental Response, Air Pollution Control Division, Water Pollution Control Division, Solid Waste Management Division, Laboratory Division, and

reduce adverse effects to the environment resulting from surface coal mining operations. It is also the intent of this act to assure that surface coal mining activities are not conducted where reclamation, as required by this law, is not feasible.

Regulations

The following rules and regulations set forth by different Alabama state agencies may have a significant impact to the siting of an oil shale plant:

Department of Conservation and Natural Resources:

Alabama Abandoned Mine Reclamation Act

Department of Environmental Management of Surface Mining Regulations
(Division 6 of Water Quality Program):

Alabama Mine Drainage Regulations

Section 6-9-.03: Pollutant Abatement and/or Prevention Plan

Guidelines for Minimizing The Effects on Surface Mining and Surface Effects of Underground Mining on Water Quality Surface Mining Commission Rules and Regulations:

Alabama Surface Mining and Reclamation Rules

Chapter 880-X-7: Areas Unsuitable for Mining

Section A: General

Section B: Areas Designated by the Act

Section C: Criteria for Designating Areas as Unsuitable for Surface Coal Mining Operations

Section D: State Processes for Designating Areas Unsuitable for Surface Coal Mining Operations

Chapter 880-X-10: Performance Standards

Section A: Performance Standards -- General

Section B: Performance Standards -- Coal Exploration

Section C: Performance Standards -- Surface Mining Activities

Section D: Performance Standards -- Underground Mining Activities

Section E: Special Performance Standards -- Concurrent Surface and Underground Mining

Section J: Special Performance Standards -- Coal Processing Plants and Support Facilities Located at or Near the Mine Site but not Within the Permit Area of Mine

Indiana Wastewater Treatment Facilities Regulations

Section 2: Application and Filing Procedures for Permit
Section 4: Conditions of Approvals
Section 5: Miscellaneous Administrative Provisions.

Indiana Industrial Wastewater Pretreatment Regulations

Rule 2: Basic NPDES Requirement
Rule 4: Underground Injections
Rule 12: Standards.

Legislative History

The legislative history of the Indiana Water Pollution Control Law is as follows:

Enacted by Indiana Acts of 1945, Chapter 132
Amended by Indiana Acts of 1957, Chapter 64, 152
Amended by Indiana Acts of 1967, Chapter 273
Amended by Indiana Acts of 1971, PL 174, 175, 176
Amended by Indiana Acts of 1972, PL 97
Amended by Indiana Acts of 1973, PL 117
Amended by Indiana Acts of 1978, PL 2, 74
Amended by Indiana Acts of 1981, PL 33
Amended by Indiana Acts of 1985, PL 143
Amended by Indiana Acts of 1986, PL 112
Amended by Indiana Acts of 1987, PL 2, 34, 160, 161
Amended by Indiana Acts of 1988, PL 109.

Responsible State Agency

The following state agencies have the primary responsibilities to implementing the intent of this law:

Water Pollution Control Board. The Indiana Water Pollution Control Law creates the Water Pollution Control Board. The Water Pollution Control Board is authorized to adopt, modify, and repeal the rules, regulations, standards, and criteria set forth by this law. The board is empowered by the Indiana Wastewater Management Law to review siting plans and issue NPDES licenses and permits for land application of wastewater, construction of water pollution treatment, and control facilities.

Department of Environmental Management. Under Chapter 2 of the IEMA (IC 13-7), the DEM was created within the executive branch of the state government. The Water Pollution Control Agency of the department is charged with the responsibility to oversee and monitor the implementation and the intent of this law.

References

1. Environment Reporter, State Water Laws, Vol. 1, 1989.
2. Communication with Peter Rekins, Indiana Commerce Center, Indiana Department of Commerce, July 1989 -- April 1990.

Administrative Services Division. The following agencies from their respective divisions are designed to monitor and implement all aspects of the federal environmental laws:

1. Office of Water Management. This office is responsible for the Federal Water Pollution Control Act (also known as the CWA) and the SDWA.
2. Office of Solid Waste Management. This office is responsible for the RCRA.
3. Office of Air Management. This office is responsible for the CAA.

Section 8 of the Indiana Environmental Policy Law indicates that any state agency required by the NEPA to file a federal EIS for the EPA shall not be required to file a statement with the state government.

References

1. Environment Reporter, State Air Laws, Vol. 2, 1989.
2. Communication with Mr. Peter Rekins, Indiana Commerce Center, Indiana Department of Commerce, July 1989 -- April 1990.
3. Communication with Mr. Bruce Brown, Office of Legal Counsel, Indiana Department of Environmental Management, June 1990.

Indiana Water Pollution Control Law

Law

The purpose of the Indiana Water Pollution Control Law is to develop a comprehensive plan and program to control, prevent, and abate pollution in waters of the state with any substances deleterious to the public health. It is also the intent of this law to create an authority to oversee and develop the program and plan consistent with the intent of the SDWA and Federal Water Pollution Control Act (or known as the CWA, as amended in 1977).

Regulations

The following rules and regulations may have an indirect implication on siting an oil shale processing plant:

Indiana Water Quality Standard

Rule 1: Water Quality Standards and Minimum Treatment Requirements
Applicable to All State Waters

Section 6: Minimum Water Quality Standards

Section 7: Underground Water Standards

Section 11: Limited and Exceptional Use; Designated Water

Rule 2: Cyanides or Cyanogen Compounds; Drainage Prohibition

Rule 3: Coal Mine; Acid Mine Drainage Prohibition

Rule 7: Water Use Designations for Lake Michigan and Contiguous Harbor

Rule 8: Nondegradation of Waters for Grand Calumet River and Indiana Harbor

Rule 9: Migration Routine; Criteria.

Article 8: Volatile Organic Compound Rules

Rule 4: Petroleum Sources

Rule 6: Organic Solvent Emission Limitations.

Article 9: Carbon Monoxide Emission Rules

Rule 1: Carbon Monoxide Emission Limits

Article 12: New Source Performance Standards

Article 14: Emission Standards for Hazardous Air Pollutants

Article 16: State Environmental Policy

Rule 1: Environmental Assessment

Rule 2: Environmental Impact Statement.

Legislative History

The legislative history of the Indiana Air Pollution Control Law is as follows:

Enacted by Indiana Acts of 1961, Chapter 171
Amended by Indiana Acts of 1969, Chapter 357
Amended by Indiana Acts of 1978, PL 2
Amended by Indiana Acts of 1981, PL 24, 33, 145
Amended by Indiana Acts of 1983, PL 162
Amended by Indiana Acts of 1984, PL 83
Amended by Indiana Acts of 1985, PL 143
Amended by Indiana Acts of 1986, PL 88, 110
Amended by Indiana Acts of 1987, PL 160
Amended by Indiana Acts of 1988, PL 101
Amended by Indiana Acts of 1989, PL 123.

Responsible State Agency

The following state agencies have the primary responsibilities to implement the intent of this law:

Air Pollution Control Board. Under Section 3 of the Indiana Air Pollution Control Law, the Air Pollution Control Board was established. The Air Pollution Control Board is authorized to set rules, regulations, and standards in reference to the intent of the Federal CAA.

Department of Environmental Management. Under Section 5 of the Indiana Air Pollution Control Law, the Air Pollution Control Board is empowered to adopt rules and regulations to classify regions into attainment and nonattainment areas for regulated air pollutants based upon scientific study of geographical, topographical, and meteorological data as well as the ambient air quality standards set forth by this law.

Administrative Services Division. The following agencies from their respective divisions are designed to monitor and implement all aspects of the federal environmental laws:

1. Office of Water Management. This office is responsible for the Federal Water Pollution Control Act (also known as the CWA) and the SDWA.
2. Office of Solid Waste Management. This office is responsible for the RCRA.
3. Office of Air Management. This office is responsible for the CAA.

Section 8 of the Indiana Environmental Policy Law indicates that any state agency required by the NEPA to file a federal EIS for the EPA shall not be required to file a statement with the state government.

References

1. Environment Reporter, State Air Laws, Vol. 2, 1989.
2. Communication with Mr. Peter Rekins, Indiana Commerce Center, Indiana Department of Commerce, July 1989 -- April 1990.
3. Communication with Mr. Bruce Brown, Office of Legal Counsel, Indiana Department of Environmental Management, June 1990.

Indiana Water Pollution Control Law

Law

The purpose of the Indiana Water Pollution Control Law is to develop a comprehensive plan and program to control, prevent, and abate pollution in waters of the state with any substances deleterious to the public health. It is also the intent of this law to create an authority to oversee and develop the program and plan consistent with the intent of the SDWA and Federal Water Pollution Control Act (or known as the CWA, as amended in 1977).

Regulations

The following rules and regulations may have an indirect implication on siting an oil shale processing plant:

Indiana Water Quality Standard

Rule 1: Water Quality Standards and Minimum Treatment Requirements
Applicable to All State Waters

Section 6: Minimum Water Quality Standards

Section 7: Underground Water Standards

Section 11: Limited and Exceptional Use; Designated Water

Rule 2: Cyanides or Cyanogen Compounds; Drainage Prohibition

Rule 3: Coal Mine; Acid Mine Drainage Prohibition

Rule 7: Water Use Designations for Lake Michigan and Contiguous Harbor

Rule 8: Nondegradation of Waters for Grand Calumet River and Indiana Harbor

Rule 9: Migration Routine; Criteria.

References

1. Environment Reporter, Solid Waste and Land Laws, Vol. 2, 1989.
2. Communication with Peter Rekins, Indiana Commerce Center, Indiana Department of Commerce, July 1989 -- April 1990.
3. Communication with Mr. Bruce Brown, Office of Legal Counsel, Indiana Department of Environmental Management, June 1990.

Indiana Hazardous Waste Act

Law

The purpose of the Indiana Hazardous Waste Act is to establish policies, requirements, procedures, and standards to implement the IEMA (IC 13-7). The act also establishes a hazardous waste management program consistent with the requirement of the Federal RCRA PL, 94-580, as amended, including those amendments made by the SWDA Amendment of 1980 and regulations promulgated pursuant to RCRA. The following rules set forth by this act may have a significant impact on siting an oil shale processing plant:

Article 2: Solid Waste Management

- Rule 5: Industrial On-Site Activities Needing Permits
- Rule 9: Solid Waste Facility Classifications and Waste Criteria
- Rule 10: Siting and Design Standard Solid Waste Land Disposal Facilities
- Rule 16: Ground Water Monitoring and Corrective Action.

Regulations

The following rules and regulations may have an indirect impact on siting an oil shale processing plant:

Indiana Hazardous Waste Management Regulations

- Rule 1: Hazardous Waste Management
- Rule 3: Identification and Listing of Hazardous Waste
- Rule 5: Characteristic of Hazardous Waste
- Rule 7: Standards Applicable to Generators of Hazardous Waste
- Rule 12: Transporter of Hazardous Waste
- Rule 20: Existing Hazardous Waste Facility Standards: Groundwater Monitoring
- Rule 27: Existing Hazardous Waste Facility Standards: Land Treatment
- Rule 28: Existing Hazardous Waste Facility Standards: Landfills
- Rule 30: Existing Hazardous Waste Facility Standards: Thermal Treatment
- Rule 32: Underground Injection and Appendices.

Legislative History

The legislative history of the Indiana Hazardous Waste Act is as follows:

- Enacted by Indiana Acts of 1980, PL 103
- Amended by Indiana Acts of 1981, PL 95
- Amended by Indiana Acts of 1983, PL 171
- Amended by Indiana Acts of 1984, PL 54

References

1. Indiana Air Pollution Control Board Rules, (Recodified Version) Indiana Department of Environmental Management, September 23, 1988.
2. Indiana Air Pollution Control Board Rules, Indiana Department of Environmental Management, April 1, 1988.
3. Indiana Air Pollution Control Board Proposed Rules, Title 326 Air Pollution Control Board, LSA Document #88-89 (F), Indiana Department of Environmental Management, 1988.
4. Environment Reporter, State Air Laws, Vol. 2, 1989.
5. Communication with Peter Rekins, Indiana Commerce Center, Indiana Department of Commerce, July 1989 -- April 1990.
6. Communication with Mr. Bruce Brown, Office of Legal Counsel, Indiana Department of Environmental Management, June 1990.

Indiana Solid Waste Management Law

Law

The purpose of the Indiana Solid Waste Management Law is to establish a board known as the Solid Waste Management Board. The Board is charged with the responsibility to adopt rules to regulate the solid and hazardous wastes and atomic radiation in Indiana.

Regulations

The following rules and regulations may have an indirect impact on siting an oil shale processing plant:

Indiana Solid Waste Management Permit Regulations. This article of the regulations provides standards for approval of refusal for processing and disposal facilities as required by Section 4 of the Refuse Disposal Act (IC 36-9-30 & 31), as amended. The regulations are provided for the issuance of construction plan permits. The regulations specify minimum operating standards for such facilities and provide for the issuance of operating permits.

Legislative History

The legislative history of the Indiana Solid Waste Management Law is as follows:

Enacted by Indiana Acts of 1985, PL 143
Amended by Indiana Acts of 1987, PL 160
Amended by Indiana Acts of 1988, PL 103.

Responsible State Agency

The following state agency has the primary responsibility in implementing the intent of this law:

Solid Waste Management Board. The Solid Waste Management Board was established by the Indiana Environmental Management Act (IC 13-7) within the Department of Environmental Management. The Board is empowered to implement and monitor all aspects of the RCRA and SWDA.

Rule 5: Performance Standards

Rule 6: State Inspection and Enforcement Procedure.

Legislative History

The legislative history of the Indiana Surface Coal Mining and Reclamation Act is as follows:

Enacted by Indiana Acts of 1980, PL 101
Amended by Indiana Acts of 1981, PL 153
Amended by Indiana Acts of 1982, PL 106
Amended by Indiana Acts of 1983, PL 169
Amended by Indiana Acts of 1984, PL 17, 85
Amended by Indiana Acts of 1985, PL 148
Amended by Indiana Acts of 1986, PL 115
Amended by Indiana Acts of 1987, PL 7, 13, 165, 166, 167
Amended by Indiana Acts of 1988, PL 108, 109, 110
Amended by Indiana Acts of 1989, PL 158.

Responsible State Agency

The following state agency has the primary responsibility in implementing the intent of this act:

Department of Natural Resources. Under Chapter 2 of the act, the Department of Natural Resources is charged with the regulatory responsibility to monitor and implement the intent of this act.

References

1. Environment Reporter, Mining, Vol. 2, 1989.
2. Communication with Peter Rekins, Indiana Commerce Center, Indiana Department of Commerce, July 1989 -- April 1990.
3. Communication with Mr. Bruce Brown, Office of Legal Counsel, Indiana Department of Environmental Management, June 1990.
4. Communication with Mr. Johnny Reising, Division of Reclamation, Indiana Department of Natural Resources, June 1990.

ADDRESSES OF THE STATE AGENCIES

State Unit

INDIANA WATER POLLUTION CONTROL LAW
INDIANA WASTEWATER MANAGEMENT LAW
INDIANA AIR POLLUTION CONTROL LAW
INDIANA SOLID WASTE MANAGEMENT LAW
INDIANA HAZARDOUS WASTE ACT
INDIANA REFUSE DISPOSAL ACT

Indiana Department of Environmental Management
Office of Legal Counsel
105 South Meridian Street
Indianapolis, Indiana 46225
Contact: Mr. Bruce Brown
Phone: (317) 232-8603

References

1. Indiana Air Pollution Control Board Rules, (Recodified Version) Indiana Department of Environmental Management, September 23, 1988.
2. Indiana Air Pollution Control Board Rules, Indiana Department of Environmental Management, April 1, 1988.
3. Indiana Air Pollution Control Board Proposed Rules, Title 326 Air Pollution Control Board, LSA Document #88-89 (F), Indiana Department of Environmental Management, 1988.
4. Environment Reporter, State Air Laws, Vol. 2, 1989.
5. Communication with Peter Rekins, Indiana Commerce Center, Indiana Department of Commerce, July 1989 -- April 1990.
6. Communication with Mr. Bruce Brown, Office of Legal Counsel, Indiana Department of Environmental Management, June 1990.

Indiana Solid Waste Management Law

Law

The purpose of the Indiana Solid Waste Management Law is to establish a board known as the Solid Waste Management Board. The Board is charged with the responsibility to adopt rules to regulate the solid and hazardous wastes and atomic radiation in Indiana.

Regulations

The following rules and regulations may have an indirect impact on siting an oil shale processing plant:

Indiana Solid Waste Management Permit Regulations. This article of the regulations provides standards for approval of refusal for processing and disposal facilities as required by Section 4 of the Refuse Disposal Act (IC 36-9-30 & 31), as amended. The regulations are provided for the issuance of construction plan permits. The regulations specify minimum operating standards for such facilities and provide for the issuance of operating permits.

Legislative History

The legislative history of the Indiana Solid Waste Management Law is as follows:

Enacted by Indiana Acts of 1985, PL 143
Amended by Indiana Acts of 1987, PL 160
Amended by Indiana Acts of 1988, PL 103.

Responsible State Agency

The following state agency has the primary responsibility in implementing the intent of this law:

Solid Waste Management Board. The Solid Waste Management Board was established by the Indiana Environmental Management Act (IC 13-7) within the Department of Environmental Management. The Board is empowered to implement and monitor all aspects of the RCRA and SWDA.

**INDIANA SOLID WASTE MANAGEMENT LAW
INDIANA HAZARDOUS WASTE ACT**

Department of Environmental Management
Office of Solid and Hazardous Waste Management
105 South Meridian Street
P.O. Box 7035
Indianapolis, Indiana 46225
Contact: Martin Harmless, Director
Phone: (317) 232-3210

INDIANA SURFACE COAL MINING AND RECLAMATION ACT

Department of Natural Resources Reclamation
Division of Reclamation
309 West Washington Street
Indianapolis, Indiana 46024
Contact: Johnny Reising, Acting Director
Phone: (317) 232-1547

Kentucky

Kentucky Environmental Protection Law (Water)

Law

The purpose of the Kentucky Environmental Protection Law (KEPL) is to conserve the public water supply by providing a comprehensive program in the public interest for the prevention, abatement, and control of any form of pollution. It is also the intent of this law to establish a department within the branch of state government to be known as the Natural Resources and Environmental Protection Cabinet to enforce and implement the intent of this law. The law also allows the cabinet to outline programs and establish state agencies to monitor and control pollution.

Regulations

The following regulations, the Kentucky Administrative Regulations (401 KAR, Chapter 5), that pertain to water pollution control could have a significant impact in siting an oil shale processing plant:

Kentucky Waste Discharge Regulations

Section 005: The Application and Preliminary Conditions for Permits to Construct Wastewater Treatment Facilities

Kentucky Water Quality Standards

Section 026: Classification of Waters
Section 028: General Provision
Section 031: Surface Water Standards
Section 035: Treatment Requirements and Compliance

INDIANA SURFACE COAL MINING AND RECLAMATION ACT

Department of Natural Resources
Division of Reclamation
309 West Washington Street
Suite 201
Indianapolis, Indiana 46204
Contact: Mr. Johnny Reising, Acting Director
Mr. Jack McGriffin
Ms. Diane Johnson
Phone: (317) 232-1547

Indiana Department of Natural Resources
Oil and Gas Division
Room 608, State Office Building
100 North Senate Avenue
Indianapolis, Indiana 46204
Contact:
Phone: (317) 232-4455

Department of Environmental Management
Technical Assistance
Chesapeake Building
105 South Meridian Street
Indianapolis, Indiana 46225
Contact:
Phone: (317) 232-8172

State Sub-unit

INDIANA WATER POLLUTION CONTROL LAW

Department of Environmental Management
Office of Water Management
Chesapeake Building
105 South Meridian Street
Indianapolis, Indiana 46225
Contact: Mr. Charlie Bardonner, Director
Phone: (317) 232-8476

INDIANA AIR POLLUTION CONTROL LAW

Department of Environmental Management
Office of Air Management
Chesapeake Building
105 South Meridian Street
Indianapolis, Indiana 46225
Contact: Mr. Tim Mathod, Director
Phone: (317) 232-5586

Department for Environmental Protection. Under KRS 224.012 of the KEPL, the Department for Environmental Protection (DEP), the Department of Natural Resources and the Department for Surface Mining Reclamation and Enforcement were established within the structure of the Natural Resources and Environmental Protection Cabinet. The DEP is empowered by the cabinet to execute the rules and regulations set forth by the federal environmental laws and adopted by the cabinet.

References

1. Kentucky Oil Shale Development, 2nd Printing, Kentucky Department of Energy, Office of Policy and Evaluation, 1982.
2. Regulations for Oil Shale Operations, Department of Surface Mining Reclamation and Enforcement, 1983.
3. Environment Reporter, State Water Laws, Vol. 1, 1989.
4. Communication with Mr. James Hale, Division of Permits, Department for Surface Mining Reclamation and Enforcement, Technical Service Branch, Natural Resources and Environmental Protection Cabinet, July 1989 -- June 1990.
5. Communication with Ms. Brenda Hartley, Manager of Permit Review Branch, Department for Surface Mining Reclamation and Enforcement, Natural Resources and Environmental Protection Cabinet, January -- June 1990.
6. Communication with Mr. Jack A. Wilson, Division of Water, Natural Resources and Environmental Agency, June 1990.

Kentucky Environmental Protection Law (Air)

Law

The purpose of the KEPL is to conserve the public water supply by providing a comprehensive program in the public interest for the prevention, abatement, and control of any form of pollution. It is also the intent of this law to establish a department within the branch of state government to be known as the Natural Resources and Environmental Protection Cabinet to enforce and implement the intent of this law. The law also allows the cabinet to outline programs and establish state agencies to monitor and control pollution.

Regulations

The following regulations, the Kentucky Administrative Regulations (401 KAR, Chapter 50-60), that pertain to air pollution control could have a significant impact on siting an oil shale processing plant:

Kentucky Air Pollution Control Regulations

- 401 KAR 50:015: Documents Incorporated by Reference
- 401 KAR 50:020: Air Quality Control Regions
- 401 KAR 50:035: Permits
- 401 KAR 50:040: Air Quality Models
- 401 KAR 51:010: Attainment Status Designation
- 401 KAR 51:017: Prevention of Significant Deterioration
- 401 KAR 53 010: Ambient Air Quality Standards
- 401 KAR 59:010: New Process Operations
- 401 KAR 59:045: New Petroleum Refineries

INDIANA SURFACE COAL MINING AND RECLAMATION ACT

Department of Natural Resources
Division of Reclamation
309 West Washington Street
Suite 201
Indianapolis, Indiana 46204
Contact: Mr. Johnny Reising, Acting Director
Mr. Jack McGriffin
Ms. Diane Johnson
Phone: (317) 232-1547

Indiana Department of Natural Resources
Oil and Gas Division
Room 608, State Office Building
100 North Senate Avenue
Indianapolis, Indiana 46204
Contact:
Phone: (317) 232-4455

Department of Environmental Management
Technical Assistance
Chesapeake Building
105 South Meridian Street
Indianapolis, Indiana 46225
Contact:
Phone: (317) 232-8172

State Sub-unit

INDIANA WATER POLLUTION CONTROL LAW

Department of Environmental Management
Office of Water Management
Chesapeake Building
105 South Meridian Street
Indianapolis, Indiana 46225
Contact: Mr. Charlie Bardonner, Director
Phone: (317) 232-8476

INDIANA AIR POLLUTION CONTROL LAW

Department of Environmental Management
Office of Air Management
Chesapeake Building
105 South Meridian Street
Indianapolis, Indiana 46225
Contact: Mr. Tim Mathod, Director
Phone: (317) 232-5586

References

1. Kentucky Oil Shale Development, 2nd Printing, Kentucky Department of Energy, Office of Policy and Evaluation, 1982.
2. Regulations for Oil Shale Operations, Department of Surface Mining Reclamation and Enforcement, 1983.
3. Environment Reporter, State Air Laws, Vol. 2, 1989.
4. Communication with Mr. James Hale, Division of Permits, Department for Surface Mining Reclamation and Enforcement, Technical Service Branch, Natural Resources and Environmental Protection Cabinet, July 1989 -- June 1990.
5. Communication with Ms. Brenda Hartley, Manager of Permit Review Branch, Department for Surface Mining Reclamation and Enforcement, Natural Resources and Environmental Protection Cabinet, January -- June 1990.
6. Communication with Hisham M. Saa'id, Acting Director, Division of Air Quality, Department of Environmental Protection, June 1990.

Kentucky Environmental Protection Law (Waste)

Law

The purpose of the KEPL is to conserve the public water supply by providing a comprehensive program in the public interest for the prevention, abatement, and control of any form of pollution. It is also the intent of this law to establish a department within the branch of state government to be known as the Natural Resources and Environmental Protection Cabinet to enforce and implement the intent of this law. The law also allows the cabinet to outline programs and establish state agencies to monitor and control pollution.

Regulations

The following regulations, the Kentucky Administrative Regulations (401 KAR, Chapter 30-49), that pertain to waste management could have a significant impact on siting an oil shale processing plant:

Kentucky Waste Management Rules

- 401 KAR 47:030: Environmental Performance Standards
- 401 KAR 31:010: General Provisions for Hazardous Waste
- 401 KAR 31:020: Criteria for Identifying the Characteristics of Hazardous Waste and Criteria for Listing
- 401 KAR 31:030: Characteristic of Hazardous Waste
- 401 KAR 31:040: Lists of Hazardous Waste
- 401 KAR 34:020: General Facility Standards.

Legislative History

The legislative history of the KEPL consists of several sections of major amendment. The amendments pertaining to solid waste management are summarized as follows:

Enacted by Acts of 1968, Chapter 82
Amended by Acts of 1972, Chapter 3

401 KAR 59:049: New Petroleum Refinery Equipment Leaks
401 KAR 59:050: New Storage Vessels for Petroleum Liquids
401 KAR 59:052: New Volatile Organic Liquid Storage Vessel
401 KAR 59:105: New Process Gas Stream
401 KAR 63:010: Fugitive Emissions
401 KAR 63:015: Flares.

Regarding 401 KAR 51:010, the U.S. EPA has reclassified Jefferson County as attainment for carbon monoxide, and the process of amending this regulation through the legislative process is now underway. Further, pursuant to KRS Chapter 77, the Air Pollution Control District of Jefferson County has concurrent jurisdiction for the control of sources in Jefferson County (Louisville) and maintains its own legally enforceable regulations.

Legislative History

The legislative history of the KEPL consists of several sections of major amendment. The amendments pertaining to air pollution control and abatement are summarized as follows:

Enacted by Acts of 1950, Chapter 69
Amended by Acts of 1952, Chapter 127
Amended by Acts of 1958, Chapter 148
Amended by Acts of 1962, Chapter 174
Amended by Acts of 1966, Chapter 21, 22
Amended by Acts of 1968, Chapter 82
Amended by Acts of 1970, Chapter 5, 92, 153, 230
Amended by Acts of 1972, Chapter 3
Amended by Acts of 1974, Chapter 74, 99, 137, 355
Amended by Acts of 1976, Chapter 289, 290, 299
Amended by Acts of 1978, Chapter 113, 117, 119, 154, 155, 207, 257, 266
Amended by Acts of 1980, Chapter 196, 264, 284, 377
Amended by Acts of 1982, Chapter 22, 74, 145, 192
Amended by Acts of 1984, Chapter 111, 369
Amended by Acts of 1986, Chapter 172, 237, 331, 455
Amended by Acts of 1988, Chapter 413.

Responsible State Agency

The following state agencies have the primary responsibilities to implement and monitor the intent of the law:

Air Pollution Agency. Section .033 and .037 of the KEPL designates the cabinet as the Air Pollution Agency for any city, district, or authority within the state for all purposes of the Federal Air Quality Act (PL 90-148), as amended.

Department for Environmental Protection. Under KRS 224.012 of the KEPL, the DEP, the Department of Natural Resources, and the Department for Surface Mining Reclamation and Enforcement are established within the structure of the Natural Resources and Environmental Protection Cabinet. The DEP is empowered by the cabinet to execute the rules and regulations set forth by the federal environmental laws and adopted by the cabinet.

Kentucky Surface Mining Law (Coal, Oil Shale, Limestone, etc.)

Law

The purpose of the Kentucky Surface Mining Law is to protect the public and the environment from the adverse effects of mining. Such impacts include soil erosion, damage from rolling stones and overburden, landslides, stream pollution, accumulation of stagnant water, and seepage of contaminated water. Land reclamation is another primary objective of this law. It is the intent of this law to establish the Department of Surface Mining Reclamation and Enforcement to oversee the law. While much of KRS Chapter 350 deals with coal mining, the following sections, especially Section 600, of this law could have a significant impact on siting an oil shale plant:

Section 350.028: Powers of Cabinet
Section 350.050: Powers of Cabinet
Section 350.151: Promulgation of Permanent Program Administrative Regulations for Mining and Reclamation; Bond
Section 350.600: Legislative Findings and Intent; Commercial Oil Shale Mining Prohibited Until Adoption of Rules and Regulations.

Regulations

The following regulations could have a direct impact on siting an oil shale processing plant:

Regulations for Oil Shale Operations (405 KAR Chapter 30)

Section 090: General Provisions for Inspection and Enforcement
Section 121: Oil Shale Exploration
Section 125: Oil Shale Exploration Performance Standards
Section 130: Oil Shale Operation Permits
Section 220: Post-Mining Land Use
Section 230: Air Resources Protection
Section 240: Protection of Fish, Wildlife, and Related Environmental Values
Section 260: Access Roads, Haul Roads, Overland Conveyor Systems, Pipeline, and Other Transportation Facilities
Section 270: Casing and Sealing of Drilled Holes
Section 300: Protection of Hydrologic System
Section 310: Diversion of Flows and Water Withdrawal
Section 320: Water Quality Standards, Effluent Limitations, and Monitoring
Section 340: Leachate Control
Section 350: Permanent Impoundments
Section 360: Waste Management Provisions
Section 370: Disposal of Excess Spoil Materials and Spent Shale
Section 390: Backfilling and Grading
Section 400: Revegetation
Section 410: In Situ Operations.

401 KAR 59:049: New Petroleum Refinery Equipment Leaks
401 KAR 59:050: New Storage Vessels for Petroleum Liquids
401 KAR 59:052: New Volatile Organic Liquid Storage Vessel
401 KAR 59:105: New Process Gas Stream
401 KAR 63:010: Fugitive Emissions
401 KAR 63:015: Flares.

Regarding 401 KAR 51:010, the U.S. EPA has reclassified Jefferson County as attainment for carbon monoxide, and the process of amending this regulation through the legislative process is now underway. Further, pursuant to KRS Chapter 77, the Air Pollution Control District of Jefferson County has concurrent jurisdiction for the control of sources in Jefferson County (Louisville) and maintains its own legally enforceable regulations.

Legislative History

The legislative history of the KEPL consists of several sections of major amendment. The amendments pertaining to air pollution control and abatement are summarized as follows:

Enacted by Acts of 1950, Chapter 69
Amended by Acts of 1952, Chapter 127
Amended by Acts of 1958, Chapter 148
Amended by Acts of 1962, Chapter 174
Amended by Acts of 1966, Chapter 21, 22
Amended by Acts of 1968, Chapter 82
Amended by Acts of 1970, Chapter 5, 92, 153, 230
Amended by Acts of 1972, Chapter 3
Amended by Acts of 1974, Chapter 74, 99, 137, 355
Amended by Acts of 1976, Chapter 289, 290, 299
Amended by Acts of 1978, Chapter 113, 117, 119, 154, 155, 207, 257, 266
Amended by Acts of 1980, Chapter 196, 264, 284, 377
Amended by Acts of 1982, Chapter 22, 74, 145, 192
Amended by Acts of 1984, Chapter 111, 369
Amended by Acts of 1986, Chapter 172, 237, 331, 455
Amended by Acts of 1988, Chapter 413.

Responsible State Agency

The following state agencies have the primary responsibilities to implement and monitor the intent of the law:

Air Pollution Agency. Section .033 and .037 of the KEPL designates the cabinet as the Air Pollution Agency for any city, district, or authority within the state for all purposes of the Federal Air Quality Act (PL 90-148), as amended.

Department for Environmental Protection. Under KRS 224.012 of the KEPL, the DEP, the Department of Natural Resources, and the Department for Surface Mining Reclamation and Enforcement are established within the structure of the Natural Resources and Environmental Protection Cabinet. The DEP is empowered by the cabinet to execute the rules and regulations set forth by the federal environmental laws and adopted by the cabinet.

4. Steven D. Taylor, "Regulations for Oil Shale Operations in Kentucky," Eastern Oil Shale Symposium Proceedings, Kentucky, 1982.
5. Joseph J. Zaluski and Steven G. Kinkel, "A Comparison of Proposed Oil Shale Regulations with Coal Mining Regulations," Eastern Oil Shale Symposium Proceedings, Kentucky, 1981.
6. Environment Reporter, State Law, Mining, Vol. 2, 1989.
7. Communication with Mr. James Hale, Division of Permits, Department for Surface Mining Reclamation and Enforcement, Technical Service Branch, Natural Resources and Environmental Protection Cabinet, July 1989 -- June 1990.
8. Communication with Ms. Brenda Hartley, Manager of Permit Review Branch, Department for Surface Mining Reclamation and Enforcement, Natural Resources and Environmental Protection Cabinet, January -- June 1990.

ADDRESSES OF THE STATE AGENCIES

Responsible State Unit

KENTUCKY ENVIRONMENTAL PROTECTION LAW
KENTUCKY SURFACE MINING LAW

Kentucky Natural Resources and Environmental Protection Cabinet
Fifth Floor
Capital Plaza Tower
Frankfort, Kentucky 40601

Kentucky Legislative Research Commission
State Capital Building
Frankfort, Kentucky 40601
Contact:
Phone: (502) 564-8100

Responsible State Sub-unit

KENTUCKY ENVIRONMENTAL PROTECTION LAW (WATER)

Department for Environmental Protection
Division of Water/Permit Branch
18 Reilly Road
Frankfort, Kentucky 40601
Contact: Mr. Jack Wilson, Director
Mr. Doug Allgerier
Phone: (502) 564-3410, Ext. 448

KENTUCKY ENVIRONMENTAL PROTECTION LAW (AIR)

Department for Environmental Protection
Division for Air Quality
316 St. Clair Mall
Frankfort, Kentucky 40601
Contact: Mr. Hisham M. Saaïd, Acting Director
Phone: (502) 564-3382

Legislative History

The legislative history of the Kentucky Surface Mining Law is as follows:

Enacted by Laws of 1954, Chapter 8
Amended by Laws of 1956, Chapter 7
Amended by Laws of 1960, Chapter 143
Amended by Laws of 1962, Chapter 105
Amended by Laws of 1964, Chapter 61
Amended by Laws of 1966, Chapter 4, 23, 255
Amended by Laws of 1968, Chapter 152
Amended by Laws of 1972, Chapter 270, 359, 3
Amended by Laws of 1974, Chapter 69, 74, 256, 258, 315, 373, 399
Amended by Laws of 1976, Chapter 140, 289, 291, 322, 341
Amended by Laws of 1978, Chapter 105, 141, 155, 209, 260, 330, 332
Amended by Laws of 1979, Chapter 26
Amended by Laws of 1980, Chapter 62, 114, 209, 280, 283, 377
Amended by Laws of 1982, Chapter 55, 150, 192, 266, 283, 368, 409
Amended by Laws of 1984, Chapter 111, 145, 180, 190, 257, 281, 282, 328, 358, 390, 392
Amended by Laws of 1986, Chapter 64, 137, 148, 266, 331, 394, 400, 448, 451
Amended by Laws of 1988, Chapter 350.

Responsible State Agency

The following state agencies have the primary responsibilities to implement and monitor the intent of the law:

Surface Mining Agency. Section .020 of the Kentucky Surface Mining Law (KRS Chapter 350) designates the cabinet as the Surface Mining Agency for the state.

Department for Surface Mining Reclamation and Enforcement. Under KRS 224.012 of the KEPL, the Department for Surface Mining Reclamation and Enforcement, the Department of Natural Resources, and the DEP are established within the structure of the Natural Resources and Environmental Protection Cabinet. The DEP is empowered by the cabinet to execute the rules and regulations set forth by the federal environmental laws and adopted by the cabinet. The Department for Surface Mining Reclamation and Enforcement is empowered to regulate the environmental effects of oil shale mining. The Department of Surface Mining Reclamation and Enforcement has the mandate of enforcing the provisions of the oil shale regulations codified as 405 KAR Chapter.

References

1. Kentucky Surface Mining Law, Department of Surface Mining Reclamation and Enforcement, 1988.
2. Kentucky Oil Shale Development, 2nd Printing, Kentucky Department of Energy, Office of Policy and Evaluation, 1982.
3. Regulations for Oil Shale Operations, Department of Surface Mining Reclamation and Enforcement, 1983.

Michigan Water Resources Commission General Rules

Part 5: Spillage of Oil and Polluting Materials

- R 323.1154: Oil Storage Facilities, Booms of Oil
- R 323.1155: Oil Storage and On Land Facilities, Surveillance
- R 323.1156: Oil Storage and Use Areas, Emergency Containment Structure
- R 323.1158: Polluting Material Storage and Use Areas, Emergency Containment Structure.

Part 21: Wastewater Discharge Permits

- R 323.2106: Permit Requirement of Dischargers
- R 323.2136: Terms and Conditions of Permit; Prohibited Discharges
- R 323.2137: Terms and Conditions of Permits; Effluent Standards and Limitations
- R 323.2138: Terms and Conditions of Permits; Consistency with Water Quality Standards
- R 323.2162: Pretreatment Program; Public Owned Treatment Work (POTW)
- R 323.2153: Point Source Discharge; Standards of Performance
- R 323.2180: Petroleum Refining Pretreatment Standards.

Part 22: Groundwater

- R 323.2204: Protected Uses
- R 323.2205: Nondegradation of Groundwaters in Usable Aquifers; Permissible and Prohibited Discharges
- R 323.2206: Regulation of Discharges
- R 323.2207: Determination of Existing Hydrological Conditions; Report
- R 323.2208: Groundwater Monitoring
- R 323.2210: Variances
- R 323.2211: Determination of Compliance.

Michigan Water Quality Standard

- R 323.1051: Dissolved Solid
- R 323.1057: Toxic Substances
- R 323.1090: Applicability of Water Quality Standards
- R 323.1098: Antidegradation
- R 323.1100: Designated Uses.

Legislative History

The legislative history of the MWRCA is as follows:

Enacted by Public Act of 1929, No. 245
Amended by Public Act of 1941, No. 131, 216
Amended by Public Act of 1949, No. 117
Amended by Public Act of 1963, No. 165
Amended by Public Act of 1965, No. 328, 405
Amended by Public Act of 1968, No. 167, 209

Legislative History

The legislative history of the Kentucky Surface Mining Law is as follows:

Enacted by Laws of 1954, Chapter 8
Amended by Laws of 1956, Chapter 7
Amended by Laws of 1960, Chapter 143
Amended by Laws of 1962, Chapter 105
Amended by Laws of 1964, Chapter 61
Amended by Laws of 1966, Chapter 4, 23, 255
Amended by Laws of 1968, Chapter 152
Amended by Laws of 1972, Chapter 270, 359, 3
Amended by Laws of 1974, Chapter 69, 74, 256, 258, 315, 373, 399
Amended by Laws of 1976, Chapter 140, 289, 291, 322, 341
Amended by Laws of 1978, Chapter 105, 141, 155, 209, 260, 330, 332
Amended by Laws of 1979, Chapter 26
Amended by Laws of 1980, Chapter 62, 114, 209, 280, 283, 377
Amended by Laws of 1982, Chapter 55, 150, 192, 266, 283, 368, 409
Amended by Laws of 1984, Chapter 111, 145, 180, 190, 257, 281, 282, 328, 358, 390, 392
Amended by Laws of 1986, Chapter 64, 137, 148, 266, 331, 394, 400, 448, 451
Amended by Laws of 1988, Chapter 350.

Responsible State Agency

The following state agencies have the primary responsibilities to implement and monitor the intent of the law:

Surface Mining Agency. Section .020 of the Kentucky Surface Mining Law (KRS Chapter 350) designates the cabinet as the Surface Mining Agency for the state.

Department for Surface Mining Reclamation and Enforcement. Under KRS 224.012 of the KEPL, the Department for Surface Mining Reclamation and Enforcement, the Department of Natural Resources, and the DEP are established within the structure of the Natural Resources and Environmental Protection Cabinet. The DEP is empowered by the cabinet to execute the rules and regulations set forth by the federal environmental laws and adopted by the cabinet. The Department for Surface Mining Reclamation and Enforcement is empowered to regulate the environmental effects of oil shale mining. The Department of Surface Mining Reclamation and Enforcement has the mandate of enforcing the provisions of the oil shale regulations codified as 405 KAR Chapter.

References

1. Kentucky Surface Mining Law, Department of Surface Mining Reclamation and Enforcement, 1988.
2. Kentucky Oil Shale Development, 2nd Printing, Kentucky Department of Energy, Office of Policy and Evaluation, 1982.
3. Regulations for Oil Shale Operations, Department of Surface Mining Reclamation and Enforcement, 1983.

- R 336.1221: Construction of Source of Particulate Matter, Sulfur Dioxides, or Carbon Monoxide in or Near Nonattainment Areas; Conditions for Approval
- R 336.1371: Required Air Quality Models

Part 3: Emission Limitations and Prohibitions -- Particulate

- R 336.1301: Standards for Density of Emission
- R 336.1331: Emission of Particulate Matter
- R 336.1371: Fugitive Dust Control Programs Other than Areas Listed in Table 36 of the Rules

Part 4: Emission Limitations and Prohibitions - Sulfur Bearing Compounds

- R 336.1430: Oil and Natural Gas Producing or Transporting Facilities and Natural Gas Processing Facilities Emissions; Operation

Part 7: Emission Limitations and Prohibitions -- New Source of Volatile Organic Compound Emissions

- R 336.1617: Existing Organic Compound-Water Separators at Petroleum Refineries
- R 336.1622: Emission of Volatile Organic Compound from Existing Component of Petroleum Refinery; Refinery Monitoring Program

Part 13: Air Pollution Episodes.

Legislative History

The legislative history of the MAPCL is as follows:

Enacted by Public Act of 1965, No. 250, 348
Amended by Public Act of 1966, No. 95, 270
Amended by Public Act of 1967, No. 97, 145
Amended by Public Act of 1972, No. 257, 330
Amended by Public Act of 1973, No. 159
Amended by Public Act of 1976, No. 100, 348
Amended by Public Act of 1977, No. 177
Amended by Public Act of 1978, No. 490
Amended by Public Act of 1981, No. 106
Amended by Public Act of 1986, No. 65
Amended by Public Act of 1987, No. 25.

Responsible State Agency

The following state agencies have the primary responsibilities to promulgate the intent of the law:

Air Pollution Control Commission. Under Section 336.13 of the MAPL, the APCC was created to administer the Air Pollution Act and Rules. The commission is empowered to set rules and standards for ambient air quality and emissions. The commission is also charged with the responsibility to set air

Amended by Public Act of 1970, No. 200
Amended by Public Act of 1972, No. 118, 129, 159, 293
Amended by Public Act of 1973, No. 3
Amended by Public Act of 1977, No. 150
Amended by Public Act of 1981, No. 116
Amended by Public Act of 1987, No. 92.

Responsible Agency

The following state agency has the primary responsibility to monitor and promulgate the intent of the act:

Water Resource Commission. Under Section 323.1 of the MWRCA, the Water Resources Commission was created within the Environmental Protection Branch of the DNR. The commission is empowered to establish water pollution standards for lakes, rivers, streams, and other waters of the state of Michigan. The commission is also authorized to issue discharge permits to assure compliance with state standards to regulate municipal, industrial, or commercial discharge or storage of any substance that may effect the quality of waters of the state.

References

1. Michigan Permit Requirements for Natural Resource Development, Department of Natural Resources, March 1986.
2. Environment Reporter, State Water Laws, Vol. 2, 1989.
3. Communication with Mr. Roger Whitener, Supervisor, Policy, Procedures and Special Services Unit, Geological Survey Division, Michigan Department of Natural Resources, September 1989 -- February 1990.
4. Communication with Ms. Donna Stine, Legislative Division, Michigan Department of Natural Resources, January 1990.
5. Communication with Ms. Joan Peck, Chief, Groundwater Management Division, Michigan Department of Natural Resources, June 1990.

Michigan Air Pollution Control Laws

Law

The purpose of the Michigan Air Pollution Law (MAPL), or generally known as the Air Pollution Act, is to develop a comprehensive program to prevent any form of deterioration of air quality, air contamination, and air pollution. It is also the intent of this law to establish an Air Pollution Control Commission (APCC) to implement the objectives of the law.

Regulations

The following regulations, rules, and standards promulgated by the law may have significant impact on siting an oil shale plant:

Michigan Administrative Rules for Air Pollution Control

Part 2: Air Use Approval

R 336.1220: Construction of Source of Volatile Compounds in Ozone Nonattainment Areas; Conditions and Approval

Part 3: Generator of Hazardous Waste

- R 299.9302: Hazardous Waste Determination and Level of Management
- R 299.9305: Pre-Transport Requirements
- R 299.9311: Land Disposal Restrictions

Part 4: Transporters of Hazardous Waste

- R 299.9410: Hazardous Waste Discharge

Part 5: Construction Permits and Operation Licenses

- R 299.9505: Linear Systems for Landfills, Surface Impoundments, and Waste Piles

Part 6: Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities

- R 299.960: Applicability; Relationship to Interim State Standards
- R 299.9602: Environmental and Human Health Standards Generally
- R 299.9603: Location Standards
- R 299.9611: Environmental Monitoring
- R 299.9612: Groundwater Monitoring.

Legislative History

The legislative history of the MHWMA is as follows:

- Enacted by Public Act of 1979, No. 64
- Amended by Public Act of 1980, No. 301
- Amended by Public Act of 1981, No. 64
- Amended by Public Act of 1982, No. 486
- Amended by Public Act of 1984, No. 412
- Amended by Public Act of 1987, No. 167, 195, 228, 246
- Amended by Public Act of 1989, No. 53.

Responsible State Agency

The following state agencies have the primary responsibilities to set policies, rules, and regulations and to promulgate and monitor the intent of this act:

Department of Natural Resources. The DNR is charged with the responsibility to implement the intent of the act. The department is also in charge of monitoring the promulgation of the regulations and rules.

Hazardous Waste Policy Committee. Under Section 299.508 of the MHWMA, the Hazardous Waste Policy Committee was created in the DNR. The committee is charged with the responsibility to prepare updated state hazardous waste management plans. The Commission of Natural Resources, with the advice of the Director of Public Health, adopts or rejects the updated plans upon the recommendation of the Hazardous Waste Policy Committee.

Amended by Public Act of 1970, No. 200
Amended by Public Act of 1972, No. 118, 129, 159, 293
Amended by Public Act of 1973, No. 3
Amended by Public Act of 1977, No. 150
Amended by Public Act of 1981, No. 116
Amended by Public Act of 1987, No. 92.

Responsible Agency

The following state agency has the primary responsibility to monitor and promulgate the intent of the act:

Water Resource Commission. Under Section 323.1 of the MWRCA, the Water Resources Commission was created within the Environmental Protection Branch of the DNR. The commission is empowered to establish water pollution standards for lakes, rivers, streams, and other waters of the state of Michigan. The commission is also authorized to issue discharge permits to assure compliance with state standards to regulate municipal, industrial, or commercial discharge or storage of any substance that may effect the quality of waters of the state.

References

1. Michigan Permit Requirements for Natural Resource Development, Department of Natural Resources, March 1986.
2. Environment Reporter, State Water Laws, Vol. 2, 1989.
3. Communication with Mr. Roger Whitener, Supervisor, Policy, Procedures and Special Services Unit, Geological Survey Division, Michigan Department of Natural Resources, September 1989 -- February 1990.
4. Communication with Ms. Donna Stine, Legislative Division, Michigan Department of Natural Resources, January 1990.
5. Communication with Ms. Joan Peck, Chief, Groundwater Management Division, Michigan Department of Natural Resources, June 1990.

Michigan Air Pollution Control Laws

Law

The purpose of the Michigan Air Pollution Law (MAPL), or generally known as the Air Pollution Act, is to develop a comprehensive program to prevent any form of deterioration of air quality, air contamination, and air pollution. It is also the intent of this law to establish an Air Pollution Control Commission (APCC) to implement the objectives of the law.

Regulations

The following regulations, rules, and standards promulgated by the law may have significant impact on siting an oil shale plant:

Michigan Administrative Rules for Air Pollution Control

Part 2: Air Use Approval

R 336.1220: Construction of Source of Volatile Compounds in Ozone Nonattainment Areas; Conditions and Approval

Department of Natural Resources. Under Section 299.408 of the MSWMA, the DNR and a Public Health Department officer assist in developing and encouraging methods for the disposal of solid waste. Section 299.412 allows the department to issue solid waste site construction permits. The department will not license a landfill facility to operate if the facility has not adopted an operating hydrogeologic monitoring program.

References

1. Michigan's Solid Waste Management Act, Act No. 641, P.A. 1978 As Amended by Act No. 10, P.A. 1979 and Act No. 88, P.A. 1981.
2. Environment Reporter, State Solid Waste and Land Use Laws, Vol. 3, 1989.
3. Michigan Permit Requirements for Natural Resource Development, Department of Natural Resources, March 1986.
4. Communication with Mr. Roger Whitener, Supervisor, Policy, Procedures and Special Services Unit, Geological Survey Division, Michigan Department of Natural Resources, September 1989 -- February 1990.
5. Communication with Ms. Donna Stine, Legislative Division, Michigan Department of Natural Resources, January 1990.

Michigan Resource Recovery Act

Law

The purpose of the Michigan Resource Recovery Act (MRRA) is to encourage the conservation of natural resources through the promotion or development of systems to collect, separate, reclaim, and recycle metals, glass, paper, and other materials of value from waste and for energy production uses. The act also provides a coordinated statewide waste management and resource recovery program.

Regulations

The following rules set forth by the MRRA could have an impact on siting an oil shale plant:

Michigan Resource Recovery Commission Rules

Legislative History

The legislative history of the MRRA is as follows:

Enacted by Public Act of 1974, No. 366
Amended by Public Act of 1977, No. 178
Amended by Public Act of 1983, No. 65.

Responsible State Agency

The following state agency has the primary responsibility to promulgate and monitor the intent of the act:

State Resource Recovery Commission. Under Section 7 of the MRRA, the State Resource Recovery Commission was established within the Environmental Protection Branch of the DNR. The commission is empowered to adopt or review

Site Review Board. Under Section 299.517 of the MHWMA, a Site Review Board was created to review and grant or deny final approval for each hazardous site construction permit application.

References

1. Rules for Hazardous Waste Management, Waste Management Division, Michigan Department of Natural Resources, 1989.
2. Environment Reporter, State Solid Waste and Land Use Laws, Vol. 3, 1989.
3. Michigan Permit Requirements for Natural Resource Development, Department of Natural Resources, March 1986.
4. Communication with Mr. Roger Whitener, Supervisor, Policy, Procedures and Special Services Unit, Geological Survey Division, Michigan Department of Natural Resources, September 1989 -- February 14, 1990.
5. Communication with Ms. Donna Stine, Legislative Division, Michigan Department of Natural Resources, January 5, 1990.
6. Communication with Mr. Kenneth J. Burda, Chief, Hazardous Waste Permits Section, Waste Management Division, August -- October 1989.

Michigan Solid Waste Management Act

Law

The purpose of the Michigan Solid Waste Management Act (MSWMA) is to provide for a comprehensive plan that prevents and protects underground water sources from any form of pollution or contamination due to the failure of the underground storage tank system.

Regulation

The following rules and regulations set forth by the MSWMA could have an impact on siting an oil shale plant:

Michigan Solid Waste Management Regulations

- Part 4: Solid Waste Processing Plants
- Part 6: Solid Waste Transporting Units
- Part 7: Solid Waste Management Plans.

Legislative History

The legislative history of the MSWMA is as follows:

- Enacted by Public Act of 1978, No. 641
- Amended by Public Act of 1979, No. 10
- Amended by Public Act of 1981, No. 88
- Amended by Public Act of 1985, No. 167
- Amended by Public Act of 1987, No. 209
- Amended by Public Act of 1988, No. 6.

Responsible State Agencies

The following state agency has the primary responsibility to carry out the intent of the act:

Legislative History

The Michigan Mine Reclamation Act was enacted by P.L. of 1982, No. 303 (enrolled Senate Bill No. 819).

Responsible State Agency

The following state agencies have the primary responsibilities to monitor and promulgate the intent of this act:

Department of Natural Resources. Under Section 107 of this act, the DNR has exclusive jurisdiction over all surface coal mining and reclamation operations in the state of Michigan. The department is authorized to promulgate and enforce rules pertaining to surface coal mining and reclamation operations consistent with the general intent and purpose of this act. The department is also charged with the responsibility to issue permits and conduct, encourage, request, and participate in studies, surveys, investigations, research, experiments, training, and demonstrations in order to meet the terms of this act.

Geological Survey Division. The Geological Survey Division of the DNR is empowered by Section 2 of the rules set forth by the Mine Reclamation Act to conduct a comprehensive study and survey the mining area in order to determine the possible environmental pollution and other adverse impacts. The division is authorized by the Rule of the Mining Reclamation Act to promulgate the rules and regulations pertaining to mining operations and issuance of permits, licenses, and leases subject to mining activities.

References

1. Michigan Surface and Underground Mining Reclamation Act, Act No. 303 P.A. of 1982, (enrolled Senate Bill No. 819).
2. Michigan Mine Reclamation Act, Act No. 92 of P.A. of 1970 as Amended by Act No. 123 of P.A. of 1972.
3. Michigan Oil and Gas Regulations, Act 61 P.A. 1939 as Amended and Promulgated Rules, Act 197 P.A. of 1959, Department of Natural Resources, 1987.
4. Michigan Permit Requirements for Natural Resource Development, Department of Natural Resources, March 1986.
5. Communication with Mr. Roger Whitener, Supervisor, Policy, Procedures and Special Services Unit, Geological Survey Division, Michigan Department of Natural Resources, September 1989 -- February 1990.
6. Communication with Ms. Donna Stine, Legislative Division, Michigan Department of Natural Resources, January 1990.

ADDRESSES OF THE STATE AGENCIES

State Unit

MICHIGAN AIR POLLUTION CONTROL LAWS
MICHIGAN SURFACE AND UNDERGROUND MINE RECLAMATION ACT

Michigan Department of Natural Resources
Policy, Procedures, and Special Services Unit

Site Review Board. Under Section 299.517 of the MHWMA, a Site Review Board was created to review and grant or deny final approval for each hazardous site construction permit application.

References

1. Rules for Hazardous Waste Management, Waste Management Division, Michigan Department of Natural Resources, 1989.
2. Environment Reporter, State Solid Waste and Land Use Laws, Vol. 3, 1989.
3. Michigan Permit Requirements for Natural Resource Development, Department of Natural Resources, March 1986.
4. Communication with Mr. Roger Whitener, Supervisor, Policy, Procedures and Special Services Unit, Geological Survey Division, Michigan Department of Natural Resources, September 1989 -- February 14, 1990.
5. Communication with Ms. Donna Stine, Legislative Division, Michigan Department of Natural Resources, January 5, 1990.
6. Communication with Mr. Kenneth J. Burda, Chief, Hazardous Waste Permits Section, Waste Management Division, August -- October 1989.

Michigan Solid Waste Management Act

Law

The purpose of the Michigan Solid Waste Management Act (MSWMA) is to provide for a comprehensive plan that prevents and protects underground water sources from any form of pollution or contamination due to the failure of the underground storage tank system.

Regulation

The following rules and regulations set forth by the MSWMA could have an impact on siting an oil shale plant:

Michigan Solid Waste Management Regulations

- Part 4: Solid Waste Processing Plants
- Part 6: Solid Waste Transporting Units
- Part 7: Solid Waste Management Plans.

Legislative History

The legislative history of the MSWMA is as follows:

- Enacted by Public Act of 1978, No. 641
- Amended by Public Act of 1979, No. 10
- Amended by Public Act of 1981, No. 88
- Amended by Public Act of 1985, No. 167
- Amended by Public Act of 1987, No. 209
- Amended by Public Act of 1988, No. 6.

Responsible State Agencies

The following state agency has the primary responsibility to carry out the intent of the act:

Ohio

Ohio Water Pollution Control Act

Law

The purpose of the Ohio Water Pollution Control Act (OWPCA) is to develop a comprehensive plan and program for prevention, control, and abatement of new or existing pollution of water of the state of Ohio.

Regulations

The following regulations may have a direct impact on siting an oil shale processing plant:

Ohio Pretreatment Regulations

- 3745-3-04: Prohibited Discharges
- 3745-3-09: General Requirements Governing Application of
Ohio Categorized Pretreatment Standards
- 3745-31: Permit to Install
- 3745-36: Indirect Discharge Permit Program.

Ohio National Pollutant Discharge Elimination System Permit Regulations

- 3745-33-02: Ohio NPDES Permit Requirements
- 3745-33-05: General Permit Conditions
- 40 CFR 124: Exclusion.

Ohio Water Quality Standards

- 3745-1-04: Criteria Applicable to All Waters
- 3745-1-06: Mixing Zones
- 3745-1-07: Water Use Designation and Criteria
- 3745-1-08: Specific Zone Criteria.

Legislative History

The legislative history of the OWPCA is as follows:

- Enacted by Ohio Laws of 1951, volume 124, Page 355
- Amended by Ohio Laws 125 v 903, 130 v H 624, 131 v H 1, 132 v H 1, 132 v S 20, 132 v H 314
- Amended by Ohio Laws of 1969, S 74
- Amended by Ohio Laws of 1971, H 475
- Amended by Ohio Laws of 1972, S 397
- Amended by Ohio Laws of 1973, H 1, S 80
- Amended by Ohio Laws of 1974, H 717
- Amended by Ohio Laws of 1976, S 404
- Amended by Ohio Laws of 1978, S 445, H 513
- Amended by Ohio Laws of 1980, H 766, H 736, S 258
- Amended by Ohio Laws of 1981, S 155, H 694
- Amended by Ohio Laws of 1982, S 78, H 745, H 379, S 323

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Phone: (517) 334-6938

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State Sub-unit

MICHIGAN AIR POLLUTION CONTROL LAWS

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**MICHIGAN HAZARDOUS WASTE MANAGEMENT ACT
MICHIGAN SOLID WASTE MANAGEMENT ACT
WATER RESOURCES COMMISSION ACT**

Michigan Department of Natural Resources
Waste Management Division
Lansing, Michigan 48909
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MICHIGAN RESOURCE RECOVERY ACT

Michigan Department of Natural Resources
Resource Recovery Division
Stevens T. Mason Building
P.O. Box 30028
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MICHIGAN SURFACE AND UNDERGROUND MINE RECLAMATION ACT

Michigan Department of Natural Resources
Geological Survey Division
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Section 02: Ambient Air Quality Standards and Guidelines
Section 06: Classification of Regions
Section 07: Control of Emission of Organic Materials from Stationary Sources
Section 08: Control of Carbon Monoxide Emissions from Stationary Sources
Section 09: Control of Emission of Volatile Organic Compounds from Stationary Sources
Chapter 3745-23: Nitrogen Oxide Standards
Section 05: Classification of Regions
Section 06: Control of Nitrogen Oxides Emissions from Stationary Sources
Chapter 3745-25: Emergency Episode Standards
Section 02: Episode Criteria
Chapter 3745-31: Permit to Install New Sources of Pollution
Chapter 3745-35: Air Permits to Operate and Variances

Ohio Ambient Air Quality Standards

Chapter 3745-17: Emission of Particulate Matter
Section 02: Ambient Air Quality Standards
Section 05: Non-Degradation Policy
Section 06: Classification of Regions
Section 07: Control of Visible Particulate Emissions from Stationary Sources
Section 08: Restriction of Emissions of Fugitive Dust
Section 11: Restriction on Particulate Emission from Industrial Processes
Chapter 3745-18: Sulfur Dioxide Emission Limits
Section 07: Classification of Regions
Section 06: General Emission Limit Provisions.

Legislative History

The legislative history of the OAPCL is as follows:

Enacted by Ohio Laws of 1967, Volume 132 H 689
Amended by Ohio Laws of 1969, H 1
Amended by Ohio Laws of 1971, S 370
Amended by Ohio Laws of 1972, H 397
Amended by Ohio Laws of 1975, H 1
Amended by Ohio Laws of 1977, H 232
Amended by Ohio Laws of 1979, H 101
Amended by Ohio Laws of 1980, S 240, S 258
Amended by Ohio Laws of 1981, H 694
Amended by Ohio Laws of 1982, S 78
Amended by Ohio Laws of 1984, H 37
Amended by Ohio Laws of 1986, H 428, H 500.

Responsible State Agency

The following state agency has the primary responsibility to implement the intent of these laws:

Ohio Environmental Protection Agency. Under Section 3745.02 of the Ohio Environmental Protection Laws, the Ohio EPA was authorized to develop programs

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State Sub-unit

MICHIGAN AIR POLLUTION CONTROL LAWS

Michigan Department of Natural Resources
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Lansing, Michigan 48909
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**MICHIGAN HAZARDOUS WASTE MANAGEMENT ACT
MICHIGAN SOLID WASTE MANAGEMENT ACT
WATER RESOURCES COMMISSION ACT**

Michigan Department of Natural Resources
Waste Management Division
Lansing, Michigan 48909
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MICHIGAN RESOURCE RECOVERY ACT

Michigan Department of Natural Resources
Resource Recovery Division
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MICHIGAN SURFACE AND UNDERGROUND MINE RECLAMATION ACT

Michigan Department of Natural Resources
Geological Survey Division
Stevens T. Mason Building
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Lansing, Michigan 48909

3745-54-18: Location Standards
3745-54-90: Groundwater Protection Standards
3745-54-93: Hazardous Constituents.

Legislative History

The legislative history of the OSHWDL is as follows:

Enacted by Ohio Laws of 1967, Volume 132, H 623
Amended by Ohio Laws of 1972, S 397, H 511
Amended by Ohio Laws of 1977, H 219
Amended by Ohio Laws of 1978, S 266
Amended by Ohio Laws of 1980, S 269
Amended by Ohio Laws of 1981, S 134, H 694
Amended by Ohio Laws of 1982, S 530, S 550
Amended by Ohio Laws of 1983, H 291
Amended by Ohio Laws of 1984, H 506, H 576, H 651
Amended by Ohio Laws of 1985, H 201, H 445
Amended by Ohio Laws of 1986, H 250, H 412, H 428
Amended by Ohio Laws of 1988, H 65, H 592, S 243.

Responsible State Agency

The following state agency has the primary responsibility in implementing this law:

Ohio Environmental Protection Agency. Section 3745.02 of the OSHWL establishes the Ohio EPA. The Ohio EPA is charged with the responsibility to adopt, modify, and repeal rules and regulations that are governing the solid waste facilities in order to prevent, control, and abate pollution. Section 3745.12 of the law further empowers the Ohio EPA to establish standards, criteria, and procedures that are consistent with the Federal RCRA to monitor the solid waste pollution level in the state of Ohio.

References

1. Environment Reporter, State Solid Waste and Land Laws, Vol. 5, 1989.
2. Communication with Ms. Carol Porter, Assistant Chief, Public Interest Center, Ohio Environmental Protection Agency, January 1990.
3. Communication with Mr. K. Arthur, Division of Solid and Hazardous Waste Management, Ohio Environmental Protection Agency, June 1990.

Ohio Reclamation Law

Law

The purpose of the Ohio Reclamation Law (ORL) is to restore the area of land affected by coal mining so that it may be used for forest growth, grazing, and/or agricultural, recreational, and wildlife purposes. The law is also intended to prevent, control, and abate the placing of any sediment, solid or water borne, mining related waste into any water sources that is harmful to public health, animal life, or aquatic life.

for the prevention, control, and abatement of air pollution. The Ohio EPA is also charged with the responsibility to adopt, modify, and repeal rules prescribing ambient air quality standards for the state as a whole or for various areas of the state that are consistent with the nation's ambient air quality standards in effect under the federal CAA.

References

1. Environment Reporter, State Air Laws, Vol. 3, 1989.
2. OAC Chapter 3745-21, Carbon Monoxide, Ozone, Hydrocarbon Air Quality Standards; and Related Emission Requirements, Ohio EPA, 1988.
3. OAC Chapter 3745-17, Particulate Matter Standards, Ohio EPA, 1988.
4. OAC Chapter 3745-18, Surface Dioxide Rules, Ohio EPA, 1988.
5. OAC Chapter 3745-19, Open Burning Standards, Ohio EPA, 1988.
6. OAC Chapter 3745-23, Nitrogen Oxide Standards, Ohio EPA, 1988.
7. OAC Chapter 3745-25, Emergency Episode Standards, Ohio EPA, 1988.
8. OAC Chapter 3745-31, Permit to Install New Sources of Pollution, Ohio EPA, 1988.
9. OAC Chapter 3745-35, Air Permits to Operate and Variances, Ohio EPA, 1988.
10. Communication with Ms. Carol Porter, Assistant Chief, Public Interest Center, Ohio Environmental Protection Agency, January 3, 1990.
11. Communication with Mr. Robert Hodanbosi, Manager, Air Quality Modeling & Planning, Division of Air Pollution Control, Ohio Environmental Protection Agency, June 1990.

Ohio Solid and Hazardous Waste Disposal Law

Law

The purpose of the Ohio Solid and Hazardous Waste Disposal Law (OSHWDL) is to develop a comprehensive plan and program to prevent, control, and abate surface or subsurface discharge or migration of 1) explosive gases or leachate from a solid waste facility or 2) groundwater contamination resulting from the transfer or disposal of solid waste at a facility.

Regulations

The following rules and regulations have a direct impact on the siting of an oil shale processing plant:

Ohio Solid Waste Disposal Regulations

- 3745-27-06: Solid Waste Disposal Facility Plan Approval
- 3745-37-03: Criteria for Issuing Solid Waste Disposal Licenses

Ohio Hazardous Waste Management Regulations

- 3745-50-311: Variances from Classification as a Solid Waste
- 3745-50-312: Standards and Criteria for Variances from Classification as a Waste
- 3745-51-10: Criteria Identifying the Characteristic of Hazardous Waste
- 3745-51-11: Criteria for Listing Hazardous Waste
- 3745-52-11: Evaluating of Waste

Reclamation Review Board. Under Section 1513.05 of the ORL, the Reclamation Review Board was established. The board is authorized to review and conduct hearing issues on land reclamation and mining activities.

References

1. Ohio Surface Mine Law, Department of Natural Resources, 1985.
2. Ohio Surface Mine Rules, Department of Natural Resources, 1976.
3. Environment Reporter, State Mining Laws, Vol. 3, 1989.
4. Communication with Ms. Carol Porter, Assistant Chief, Public Interest Center, Ohio Environmental Protection Agency, January 1990.
5. Communication with Mr. Tim L. Dieringer, Chief, Division of Reclamation, Ohio Department of Natural Resources, June 1990.

Ohio Surface Mining and Reclamation Law

Law

The purpose of the Ohio Surface Mining and Reclamation Law (OSMRL) is to establish procedures and requirements for mining permits. This law also creates an authority within the Ohio DNR to promulgate the objectives of the law.

Regulations

The following regulations may have a direct impact on the siting of an oil shale processing plant:

Ohio Surface Mine Rules

- Section 14-3-02: Minimizing Acid Drainage and Acid Water Accumulation
- Section 14-3-03: Permanent Water Impoundments
- Section 14-3-05: Underground Water Supplies
- Section 14-3-06: Final Slopes
- Section 14-3-08: Resoiling
- Section 14-3-09: Soil Amendments
- Section 14-3-10: Revegetation
- Section 14-3-11: Construction of Dams, Dikes, Diversions, Impoundments, and Drainage Channels
- Section 14-4-04: Abandonment.

Legislative History

The legislative history of the OSMRL is as follows:

- Enacted by Ohio Laws of 1974, Volume 135, S 165
- Amended by Ohio Laws of 1977, S 221, 137 v S 69, H 504, 138 v H 204
- Amended by Ohio Laws of 1985, H 238, H 201
- Amended by Ohio Laws of 1987, H 88, H 231, H 457.

Responsible State Agencies

The following state agencies have the primary responsibilities to monitor and promulgate the intent of this law:

for the prevention, control, and abatement of air pollution. The Ohio EPA is also charged with the responsibility to adopt, modify, and repeal rules prescribing ambient air quality standards for the state as a whole or for various areas of the state that are consistent with the nation's ambient air quality standards in effect under the federal CAA.

References

1. Environment Reporter, State Air Laws, Vol. 3, 1989.
2. OAC Chapter 3745-21, Carbon Monoxide, Ozone, Hydrocarbon Air Quality Standards; and Related Emission Requirements, Ohio EPA, 1988.
3. OAC Chapter 3745-17, Particulate Matter Standards, Ohio EPA, 1988.
4. OAC Chapter 3745-18, Surface Dioxide Rules, Ohio EPA, 1988.
5. OAC Chapter 3745-19, Open Burning Standards, Ohio EPA, 1988.
6. OAC Chapter 3745-23, Nitrogen Oxide Standards, Ohio EPA, 1988.
7. OAC Chapter 3745-25, Emergency Episode Standards, Ohio EPA, 1988.
8. OAC Chapter 3745-31, Permit to Install New Sources of Pollution, Ohio EPA, 1988.
9. OAC Chapter 3745-35, Air Permits to Operate and Variances, Ohio EPA, 1988.
10. Communication with Ms. Carol Porter, Assistant Chief, Public Interest Center, Ohio Environmental Protection Agency, January 3, 1990.
11. Communication with Mr. Robert Hodanbosi, Manager, Air Quality Modeling & Planning, Division of Air Pollution Control, Ohio Environmental Protection Agency, June 1990.

Ohio Solid and Hazardous Waste Disposal Law

Law

The purpose of the Ohio Solid and Hazardous Waste Disposal Law (OSHWDL) is to develop a comprehensive plan and program to prevent, control, and abate surface or subsurface discharge or migration of 1) explosive gases or leachate from a solid waste facility or 2) groundwater contamination resulting from the transfer or disposal of solid waste at a facility.

Regulations

The following rules and regulations have a direct impact on the siting of an oil shale processing plant:

Ohio Solid Waste Disposal Regulations

- 3745-27-06: Solid Waste Disposal Facility Plan Approval
- 3745-37-03: Criteria for Issuing Solid Waste Disposal Licenses

Ohio Hazardous Waste Management Regulations

- 3745-50-311: Variances from Classification as a Solid Waste
- 3745-50-312: Standards and Criteria for Variances from Classification as a Waste
- 3745-51-10: Criteria Identifying the Characteristic of Hazardous Waste
- 3745-51-11: Criteria for Listing Hazardous Waste
- 3745-52-11: Evaluating of Waste

OHIO WATER POLLUTION CONTROL ACT

Ohio Environmental Protection Agency
Division of Water Pollution Control
1800 Water Mark Drive
P.O. Box 1049
Columbus, Ohio 43266-0149
Contact: Mr. George Elmaraghy, Assistant Chief
Phone: (614) 644-2001

OHIO AIR POLLUTION CONTROL LAW

Ohio Environmental Protection Agency
Division of Air Pollution Control
1800 Water Mark Drive
P.O. Box 1049
Columbus, Ohio 43266-0149
Contact: Ms. Patricia P. Walling, Chief
Phone: (614) 644-2270

Ohio Environmental Protection Agency
Air Quality Modeling and Planning
Division of Air Pollution Control
1800 Water Mark Drive
P.O. Box 1049
Columbus, Ohio 43266-0149
Contact: Mr. Robert Hodanbosi, P.E., Manager
Phone:

OHIO SOLID AND HAZARDOUS WASTE DISPOSAL LAW

Ohio Environmental Protection Agency
Division of Solid and Hazardous Waste Management
1800 Water Mark Drive
P.O. Box 1049
Columbus, Ohio 43266-0149
Contact: Mr. K. Arthur
Phone: (614) 644-2934

OHIO SURFACE MINING AND RECLAMATION LAW

Ohio Department of Natural Resources
Division of Reclamation
1855 Fountain Square Court
Building H
Columbus, Ohio 43224
Contact: Mr. Tim L. Dieringer, Chief
Phone: (614) 265-6633

Ohio Environmental Protection Agency
Public Interest Center
1800 Water Mark Drive
Columbus, Ohio 43266-0149
Phone: (614) 644-2160

Division of Reclamation. Section 1515.08 of the OSML authorizes the Division of Reclamation, which was established within the DNR, to issue mining permits and enforce coal mining laws and surface mining laws. This division is also empowered to adopt, amend, and rescind rules and procedures pertaining to permit application processes.

Reclamation Review Board. The Reclamation Review Board, established under Section 153.05 of the Ohio Law, is authorized to serve as the Reclamation Board of Review pursuant to this chapter of the law.

References

1. Ohio Surface Mine Law, Department of Natural Resources, 1985.
2. Ohio Surface Mine Rules, Department of Natural Resources, 1976.
3. Environment Reporter, Mining, Vol 3, 1989.
4. Communication with Ms. Carol Porter, Assistant Chief, Public Interest Center, Ohio Environmental Protection Agency, January 3, 1990.
5. Communication with Mr. Tim L. Dieringer, Chief, Division of Reclamation, Ohio Department of Natural Resources, June 1990.

ADDRESSES OF THE STATE AGENCIES

State Unit

OHIO ENVIRONMENTAL PROTECTION AGENCY LAW
OHIO WATER POLLUTION CONTROL ACT
OHIO AIR POLLUTION CONTROL ACT
OHIO SOLID AND HAZARDOUS WASTE DISPOSAL LAW
OHIO SURFACE MINING AND RECLAMATION ACT

Ohio Environmental Protection Agency
Legal Section
1800 Water Mark Drive
P.O. Box 1049
Columbus, Ohio 43266-0149
Contact: Mr. Alan Lapp
Phone:

OHIO SURFACE MINING AND RECLAMATION LAW

Ohio Department of Natural Resources
Fountain Square
Building B-3
Columbus, Ohio 43224

State Sub-unit

OHIO WATER DEVELOPMENT AUTHORITY ACT

Ohio Water Development Authority
50 West Board Street
Columbus, Ohio 43215

Amended by Acts of 1981, Chapter 131, 449
Amended by Acts of 1982, Chapter 917
Amended by Acts of 1983, Chapter 38
Amended by Acts of 1984, Chapter 804
Amended by Acts of 1985, Chapter 160
Amended by Acts of 1987, Chapter 111
Amended by Acts of 1988, Chapter 688, 1013
Amended by Acts of 1989, Chapter 114, 321, 591.

Responsible State Agency

The following state agency has the primary responsibility to implement the intent of the act:

Department of Health and Environment. The Department of Health and Environment is charged with the responsibility to implement and monitor the intent of this act.

Tennessee Water Control Board. Section 69-3-104 of the TWQCA established the Tennessee Water Control Board within the structure of the Department of Health and Environment. The board is authorized to adopt, modify, repeal, and promulgate necessary rules and regulations for the purpose of controlling discharge of sewage and other waste as well. The board is also empowered to adopt, amend, and revise the standards of quality for waters and issue NPDES permits.

References

1. The Tennessee Water Quality Control Act of 1977, (including the 1987 amendments), Tennessee Department of Health and Environment, 1988.
2. Rules of Tennessee Department of Health and Environment -- Bureau of Environment, Division of Water Management.
3. Communication with Mr. Larry Bowers, Department of Health and Environment, June 1990.
4. Environment Reporter, State Water Laws, Vol. 3, 1989.

Tennessee Air Quality Control Act

Law

The purpose of the Tennessee Air Quality Control Law (TAQCL) is to maintain the purity of the air resources of the state consistent with the protection of normal health, general welfare, and physical property of the people. The act seeks the accomplishment of this objective through the prevention, abatement, and control of air pollution by all practical and economically feasible methods.

Regulations

The following rules and regulations may have an indirect implication on siting an oil shale processing plant:

Division of Reclamation. Section 1515.08 of the OSML authorizes the Division of Reclamation, which was established within the DNR, to issue mining permits and enforce coal mining laws and surface mining laws. This division is also empowered to adopt, amend, and rescind rules and procedures pertaining to permit application processes.

Reclamation Review Board. The Reclamation Review Board, established under Section 153.05 of the Ohio Law, is authorized to serve as the Reclamation Board of Review pursuant to this chapter of the law.

References

1. Ohio Surface Mine Law, Department of Natural Resources, 1985.
2. Ohio Surface Mine Rules, Department of Natural Resources, 1976.
3. Environment Reporter, Mining, Vol 3, 1989.
4. Communication with Ms. Carol Porter, Assistant Chief, Public Interest Center, Ohio Environmental Protection Agency, January 3, 1990.
5. Communication with Mr. Tim L. Dieringer, Chief, Division of Reclamation, Ohio Department of Natural Resources, June 1990.

ADDRESSES OF THE STATE AGENCIES

State Unit

OHIO ENVIRONMENTAL PROTECTION AGENCY LAW
OHIO WATER POLLUTION CONTROL ACT
OHIO AIR POLLUTION CONTROL ACT
OHIO SOLID AND HAZARDOUS WASTE DISPOSAL LAW
OHIO SURFACE MINING AND RECLAMATION ACT

Ohio Environmental Protection Agency
Legal Section
1800 Water Mark Drive
P.O. Box 1049
Columbus, Ohio 43266-0149
Contact: Mr. Alan Lapp
Phone:

OHIO SURFACE MINING AND RECLAMATION LAW

Ohio Department of Natural Resources
Fountain Square
Building B-3
Columbus, Ohio 43224

State Sub-unit

OHIO WATER DEVELOPMENT AUTHORITY ACT

Ohio Water Development Authority
50 West Board Street
Columbus, Ohio 43215

Tennessee Solid Waste Disposal Act

Law

The purpose of the Tennessee Solid Waste Disposal Act (TSWDA) is to provide a coordinated statewide program to control solid waste processing and disposal activities. The comprehensive plan developed under this act is consistent with the federal regulations and allows state and local agencies to prevent, control, and abate water, air, and land pollution.

Regulations

The following rules and regulations may have an indirect impact on siting an oil shale processing plant:

Tennessee Solid Waste Regulations

- Rule 1200-1-7-.01: Solid Waste Management System
- Rule 1200-1-7-.02: Permitting of Solid Waste Processing and Disposal Facilities
- Rule 1200-1-7-.04: Specific Requirements for Class I, II, III, and IV Disposal Facilities
- Rule 1200-1-7-.05: Special Requirement for Class V Disposal Facilities
- Rule 1200-1-7-.06: Specific Requirements for Class VI Disposal Facilities

Legislative History

The legislative history of the TSWDA is as follows:

Enacted by Tennessee Public Act of 1969, Chapter 295
Amended by Acts of 1971, Chapter 100, 165
Amended by Acts of 1974, Chapter 446, 486, 666, 758, 761, 787, 799
Amended by Acts of 1975, Chapter 109, 158
Amended by Acts of 1976, Chapter 392, 427
Amended by Acts of 1978, Chapter 843
Amended by Acts of 1980, Chapter 662, 899
Amended by Acts of 1981, Chapter 131, 174
Amended by Acts of 1982, Chapter 873
Amended by Acts of 1983, Chapter 226
Amended by Acts of 1984, Chapter 965
Amended by Acts of 1985, Chapter 337
Amended by Acts of 1986, Chapter 644
Amended by Acts of 1988, Chapter 966, 967, 1013.

Responsible State Agency

The following state agency has the primary responsibility to implement the intent of this act:

Solid Waste Disposal Control Board. Section 68-31-111 of the TSWDA created the Solid Waste Disposal Control Board. The board is charged with the responsibility to adopt, modify, promulgate, and enforce the rules and regulations set forth by this act.

Tennessee Air Pollution Control Regulations

Chapter 1200-3-3: Ambient Air Quality Standards
Chapter 1200-3-5: Visible Emission
Chapter 1200-3-7: Process Emission Standards
Chapter 1200-3-9: Construction and Operation Permit
Chapter 1200-3-11: Hazardous Air Contaminants
Chapter 1200-3-14: Control of Sulfur Dioxide Emission
Chapter 1200-3-16: New Sources Performance Standards
Chapter 1200-3-18: Volatile Organic Compounds.

Legislative History

The legislative history of the TAQCA is as follows:

Enacted by Acts of 1967, Chapter 367
Amended by Acts of 1969, Chapter 89
Amended by Acts of 1970, Chapter 538, 539
Amended by Acts of 1971, Chapter 84, 108, 266, 322, 362, 365
Amended by Acts of 1972, Chapter 787
Amended by Acts of 1973, Chapter 325
Amended by Acts of 1974, Chapter 359, 598
Amended by Acts of 1975, Chapter 155, 359
Amended by Acts of 1976, Chapter 636, 639, 806
Amended by Acts of 1977, Chapter 116, 169
Amended by Acts of 1978, Chapter 894
Amended by Acts of 1979, Chapter 299, 422
Amended by Acts of 1981, Chapter 131, 449
Amended by Acts of 1984, Chapter 788
Amended by Acts of 1987, Chapter 263
Amended by Acts of 1988, Chapter 585, 1013
Amended by Acts of 1989, Chapter 321.

Responsible State Agency

The following state agency has the primary responsibility to implement the intent of this act:

Air Pollution Control Board. Under Section 68-25-104 of the TAQCA, an authority known as the Air Pollution Control Board, was established. The board is charged with the responsibility to establish, modify, amend, and promulgate rules and regulations to effect the intent and purpose of this act. The board is also empowered to review the air pollution control plans and programs recommended by the Department of Health and Environment.

References

1. Rules of Tennessee Department of Health and Environment, Bureau of Environment, Division of Air Pollution Control.
2. Communication with the Director, Tennessee Division of Air Pollution Control, June 1990.
3. Environment Reporter, State Air Laws, Vol. 4, 1989.

Amended by Acts of 1986, Chapter 528, 644, 769
Amended by Acts of 1988, Chapter 559, 578, 856
Amended by Acts of 1989, Chapter 321, 432, 552, 591.

Responsible State Agencies

The following state agencies have the primary responsibilities in implementing the intent of this act:

Department of Health and Environment. The Commissioner of the Department of Health and Environment is authorized by Section 68-46-107(a) and (b), -108, -110, and -111 of the THWMA of 1977. The department is charged with the responsibility to implement the regulatory provisions of the law including the issuance of permits to hazardous waste treatment, storage, and disposal facilities. The department is also authorized to enforce regulatory requirements and conduct compliance inspections for facilities, generators, and transporters of hazardous waste. The regulatory program is implemented primarily through the department's Division of Solid Waste Management.

Solid Waste Disposal Control Board. The Solid Waste Disposal Control Board was created under Section 68-31-111 of the TSWDA. Under Section 68-46-107(d) and (e) of the THWMA of 1977, the board is charged with the responsibility to promulgate necessary regulations to implement the THWMA of 1977, and to act as the Board of Appeals to review certain actions of the commissioner.

Reference

1. Environment Reporter, State Solid Waste and Land Laws, Vol. 6, 1989.

Tennessee Coal Surface Mining Law

Law

The purpose of the Tennessee Coal Surface Mining Law is to prevent adverse affects of the land or water resources by past coal mining practices. The law is also intended to restore, reclaim, abate, and control any form of pollution due to mining activities. In 1984, a major portion of the Tennessee Coal Surface Mining Law was repealed. However, certain sections of the act were retained by the legislature to regulate mine sites not under the jurisdiction of the federal government.

Regulations

There are presently no direct mining regulations that specifically outline the standards, criteria, and guidelines for coal and oil shale mining, processing, and marketing. However, certain sections of the rules are in effect to regulate specific mine sites.

Legislative History

The legislative history of the Tennessee Coal Surface Mining Law is as follows:

Tennessee Air Pollution Control Regulations

Chapter 1200-3-3: Ambient Air Quality Standards
Chapter 1200-3-5: Visible Emission
Chapter 1200-3-7: Process Emission Standards
Chapter 1200-3-9: Construction and Operation Permit
Chapter 1200-3-11: Hazardous Air Contaminants
Chapter 1200-3-14: Control of Sulfur Dioxide Emission
Chapter 1200-3-16: New Sources Performance Standards
Chapter 1200-3-18: Volatile Organic Compounds.

Legislative History

The legislative history of the TAQCA is as follows:

Enacted by Acts of 1967, Chapter 367
Amended by Acts of 1969, Chapter 89
Amended by Acts of 1970, Chapter 538, 539
Amended by Acts of 1971, Chapter 84, 108, 266, 322, 362, 365
Amended by Acts of 1972, Chapter 787
Amended by Acts of 1973, Chapter 325
Amended by Acts of 1974, Chapter 359, 598
Amended by Acts of 1975, Chapter 155, 359
Amended by Acts of 1976, Chapter 636, 639, 806
Amended by Acts of 1977, Chapter 116, 169
Amended by Acts of 1978, Chapter 894
Amended by Acts of 1979, Chapter 299, 422
Amended by Acts of 1981, Chapter 131, 449
Amended by Acts of 1984, Chapter 788
Amended by Acts of 1987, Chapter 263
Amended by Acts of 1988, Chapter 585, 1013
Amended by Acts of 1989, Chapter 321.

Responsible State Agency

The following state agency has the primary responsibility to implement the intent of this act:

Air Pollution Control Board. Under Section 68-25-104 of the TAQCA, an authority known as the Air Pollution Control Board, was established. The board is charged with the responsibility to establish, modify, amend, and promulgate rules and regulations to effect the intent and purpose of this act. The board is also empowered to review the air pollution control plans and programs recommended by the Department of Health and Environment.

References

1. Rules of Tennessee Department of Health and Environment, Bureau of Environment, Division of Air Pollution Control.
2. Communication with the Director, Tennessee Division of Air Pollution Control, June 1990.
3. Environment Reporter, State Air Laws, Vol. 4, 1989.

Responsible State Agencies

The following state agencies have the primary responsibilities in implementing the intent of this law:

Department of Health and Environment. The Department of Health and Environment is charged with the responsibility to implement and monitor the intent of this law.

Board of Reclamation Review. Section 59-8-321 of the Tennessee Coal Surface Mining Law established the Board of Reclamation Review within the structure of the Department of Health and Environment. The board is authorized to conduct hearings, review the Tennessee Coal Surface Mining Law and the TMSML of 1972, and recommend changes or additions in the laws as may be deemed advisable to the Governor or the General Assembly.

Reference

1. Environment Reporter, State Mining Laws, Vol. 3, 1989.

ADDRESSES OF THE STATE AGENCIES

State Unit

TENNESSEE WATER QUALITY CONTROL ACT

Department of Health and Environment
Water Quality Division
T.E.R.R.A. Building
150 Ninth Avenue North
Nashville, Tennessee 37219-5404
Contact: Mr. Larry Bower
Phone: (615) 741-7883/ (615) 741-4177

TENNESSEE AIR QUALITY ACT

Department of Health and Environment
Air Pollution Control Division
Customs House, 4th Floor
701 Broadway
Nashville, Tennessee 37219-5403
Contact: Mr. Harold E. Hodges, Director
Phone: (615) 741-3931

TENNESSEE SOLID WASTE DISPOSAL ACT TENNESSEE HAZARDOUS WASTE MANAGEMENT ACTS

Tennessee Department of Public Health
Bureau of Environmental Health Sciences
Division of Solid Waste Management
T.E.R.R.A. Building
150 Ninth Avenue North
Nashville, Tennessee 37219-5404
Contact: Mr. Larry Bower
Phone: (615) 741-7883

Enacted by Tennessee Public Act of 1980, Chapter 908
Amended by Acts of 1981, Chapter 100, 131, 169, 280, 346
Amended by Acts of 1982, Chapter 557, 779
Amended by Acts of 1983, Chapter 121, 147, 204
Amended by Acts of 1984, Chapter 837
Amended by Acts of 1987, Chapter 251.

Responsible State Agency

The following state agencies have the primary responsibilities in implementing the intent of this law:

Department of Health and Environment. The Department of Health and Environment is charged with the responsibility to implement and monitor the intent of this law.

Board of Reclamation Review. Section 59-8-321 of the Tennessee Coal Surface Mining Law established the Board of Reclamation Review within the structure of the Department of Health and Environment. The board is authorized to conduct hearings, review the Tennessee Coal Surface Mining Law and the Tennessee Minerals Surface Mining Law of 1972, and recommend changes or additions in the law as may be deemed advisable to the Governor and the General Assembly.

Reference

1. Environment Reporter, State Mining Laws, Vol. 3, 1989.

Tennessee Mineral Surface Mining Law of 1972

Law

The purpose of the Tennessee Mineral Surface Mining Law (TMSML) of 1972 is to prevent adverse affects of the land or water resources by past mineral mining practices. The law is also intended to restore and reclaim land and abate and control any form of pollution due to mining activities.

Regulations

Currently, there are regulations and rules that specifically outline the standards, criteria, and guidelines for minerals extraction by the surface mining method in Tennessee.

Legislative History

The legislative history of the TMSML is as follows:

Enacted by Tennessee Public Act of 1972, Chapter 547
Amended by Acts of 1980, Chapter 908
Amended by Acts of 1988, Chapter 1004
Amended by Acts of 1990, Chapter 890.

TASK 7. SAMPLE PROCUREMENT, PREPARATION, AND CHARACTERIZATION

The objective of this task was to procure and prepare raw and beneficiated Eastern oil shale samples for all of the experimental tasks in the program.

Subtask 7.1. Raw Shales

The objective of this task was to procure about 1,300 pounds (590 kg) of oil shale samples from Alabama, Indiana, Kentucky, Michigan, Ohio and Tennessee, and prepare these samples for beneficiation studies. Additional objectives of Task 7.1 were; 1) provide IGT with 300 to 500 pounds (136 to 227 kg) of crushed shale, which had been stored under an inert atmosphere, each year of the three year contract for PFH studies, 2) monitor chemical changes by analyses; that is, Fischer Assay oil yield, Carbon, Hydrogen, Nitrogen, Sulfur, and proximate analysis, of the samples stored under inert atmosphere for each of the three years, and 3) determine the elemental composition of the shales.

Subtask 7.1.1. Sample Procurement

Three of the six shale samples shown in Tables 7-1 through 7-6 were procured under contract from active quarries. The Kentucky sample was obtained from the Skaggs shale pit, Brooks, Kentucky, through the courtesy of the owner, Mr. Wallace Skaggs. The Ohio sample was obtained from the Galena Brick Products, Inc. pit, through the courtesy of Mr. Tom Hopper, Vice President, GID-CO, Galena, Ohio. The Michigan sample was obtained from the Lafarge Corporation, Alpena, Michigan, through the courtesy of Mr. Walter Dowd.

Table 7-1. SAMPLE DATA -- ALABAMA

State:	Alabama
Sampling Date:	April 1988
Amount:	5 tons
Shale:	Chattanooga
Member:	Undifferentiated
Age:	Devonian
County:	Madison
Quadrangle:	New Market
Type of Sample:	Outcrop

Location: The site is located two miles south of the Alabama-Tennessee state line and about 18 miles north of Huntsville. More specifically, it is along the west edge of the valley of Hester Creek in the NW of Section 18, T1S-R2E, of the New Market Quadrangle. The site was reached by walking south along the side of an embankment a distance of about 50 feet from the County highway which is the north line of Section 18.

Reference:

Rheams, K. F. and Neatherly, T. L. (1984), "Characterization and Geochemistry of Devonian Oil Shale: North Alabama, Northwest Georgian and South-central Tennessee (a resource evaluation) Final Report," DOE/LC/10937-1807, Geological Survey of Alabama, Tuscaloosa.

Enacted by Tennessee Public Act of 1980, Chapter 908
Amended by Acts of 1981, Chapter 100, 131, 169, 280, 346
Amended by Acts of 1982, Chapter 557, 779
Amended by Acts of 1983, Chapter 121, 147, 204
Amended by Acts of 1984, Chapter 837
Amended by Acts of 1987, Chapter 251.

Responsible State Agency

The following state agencies have the primary responsibilities in implementing the intent of this law:

Department of Health and Environment. The Department of Health and Environment is charged with the responsibility to implement and monitor the intent of this law.

Board of Reclamation Review. Section 59-8-321 of the Tennessee Coal Surface Mining Law established the Board of Reclamation Review within the structure of the Department of Health and Environment. The board is authorized to conduct hearings, review the Tennessee Coal Surface Mining Law and the Tennessee Minerals Surface Mining Law of 1972, and recommend changes or additions in the law as may be deemed advisable to the Governor and the General Assembly.

Reference

1. Environment Reporter, State Mining Laws, Vol. 3, 1989.

Tennessee Mineral Surface Mining Law of 1972

Law

The purpose of the Tennessee Mineral Surface Mining Law (TMSML) of 1972 is to prevent adverse affects of the land or water resources by past mineral mining practices. The law is also intended to restore and reclaim land and abate and control any form of pollution due to mining activities.

Regulations

Currently, there are regulations and rules that specifically outline the standards, criteria, and guidelines for minerals extraction by the surface mining method in Tennessee.

Legislative History

The legislative history of the TMSML is as follows:

Enacted by Tennessee Public Act of 1972, Chapter 547
Amended by Acts of 1980, Chapter 908
Amended by Acts of 1988, Chapter 1004
Amended by Acts of 1990, Chapter 890.

Table 7-3. SAMPLE DATA -- KENTUCKY

State:	Kentucky
Sampling Date:	June 1988
Amount:	5 tons
Shale:	New Albany
Member:	Clegg Creek
Age:	Mississippian
County:	Bullitt
Quadrangle:	Brooks
Type of Sample:	Outcrop

Location: Sample was taken from an active quarry located 0.8 miles south of the north line of Bullitt County some 16 miles south of the Ohio River at Louisville just off Interstate 65. On the Brooks Quadrangle the Knieriem Quarry is shown as a "shale pit" on the southeastern edge of Buttonmold Knob, 1.1 miles north-northeast of the community of Brooks.

References:

1. Kepferle, R. C., "Geologic Map of the Brooks Quadrangle, Bullitt and Jefferson Counties, Kentucky," GQ-961, U.S. Geological Survey, 1972.
2. Kepferle, R. C. and Roen J. B., "Field Trip 3 Road Log and Stop Description," in T. G. Roberts, Ed. GSA Cincinnati 1981 Field Trip Guidebooks, Vol. 11, American Geological Institute, Falls Church, VA, pp. 268-323, 1981.
3. Kepferle, R. C. and Matthews, R. D., "Field Trip Guidebook-Oil Shale and Tar Sands of Central Kentucky" in conjunction with the Synthetic Fuels from Oil Shale and Tar Sands Symposium, Louisville, Kentucky, May 17-20, 1983.
4. Robl, T. L., Barron, L. S. Koppenaal, D. W. and Bland, A. E., "The Geology and Geochemistry of Devonian Shales in South and West Central Kentucky," paper presented at the Proceedings 1983 Eastern Oil Shale Symposium, Lexington, Kentucky, November 13-16, 1983.

Table 7-2. SAMPLE DATA -- INDIANA

State: Indiana
Sampling Date: Unknown, DOE Oil Shale Sample Bank Sample
Amount: 6 tons
Shale: New Albany, DOE Oil Shale Sample Bank, Reference E-88
Member: Clegg Creek
Age: Devonian
County: Clark
Quadrangle: Unknown
Type of Sample: Outcrop

Location: Reference shale E-88 was taken from the top of an exposure of New Albany shale located on the Donald McRae farm in Clark County, Indiana. The site is approximately 25 miles north of the Ohio River at Louisville, Kentucky. The McRae farm is located on Beagle Club Road, approximately 2 miles east of Indiana Route (31). Beagle Club Road is located approximately 1 mile south of the town of Underwood, Indiana.

References:

1. Hasenmueller, N. R., "Resource Assessment of the New Albany Shale (Devonian-Mississippian) in southeastern Indiana-Preliminary Report," in Proceedings for the 1981 Eastern Oil Shale Symposium, pp. 173-180, Lexington, Kentucky.
2. Hasenmueller, N. R. and Bassett, J. L., "Stratigraphy" in N.R. Hasenmueller, and G.S. Woodard, Eds., Studies of the New Albany Shale (Devonian and Mississippian) and Equivalent Strata in Indiana, Indiana Geological Survey, for U.S. DOE/METC/05204-1128, pp. 5-32.

Table 7-6. SAMPLE DATA -- TENNESSEE

State:	Tennessee
Sampling Date:	January 1989
Amount:	1 ton
Shale:	Chattanooga
Member:	Unknown
Age:	Devonian
County:	Davidson
Quadrangle:	Unknown
Type of Sample:	Outcrop

Location: The sample was taken from a 10 foot outcrop located at mile marker 192 on Interstate Highway 40 west of Nashville, Tennessee.

Reference:

Mountain States Research and Development, and Toups Corporation, "Engineering Assessment and Feasibility Study of Chattanooga Shale as a Future Source of Uranium." June 1978.

The Indiana sample was obtained from Terra Tek, Inc., Salt Lake City, Utah. Terra Tek was the contractor for the Department of Energy's (DOE) oil shale sample bank program, (DOE Contract Number: DE-AC21-85LC11061). The Alabama sample was obtained through the courtesy of Mr. Jeff Meadows, owner of the property in Madison County, Alabama; the sample was procured by a private contractor, Ashburn and Gray, Inc., Huntsville, Alabama. The Tennessee sample was procured by MRI staff.

Subtask 7.1.2. Sample Characterization

The large-tonnage samples from Alabama and Kentucky sample were jaw-crushed to approximately 1 inch (2.5 cm) and representative samples were taken for further crushing to about 6 mesh. The smaller tonnage samples were crushed to pass 6 mesh, and all of the -6 mesh shale samples were split for periodic, or annual, shipment to IGT for hydroretorting studies. Samples of each of the -6 mesh shales scheduled for annual shipment to IGT were stored in sealed epoxy-lined drums under a nitrogen atmosphere. Representative fractions from each of the shale samples shipped annually were Fischer Assayed for oil yield and analyzed for carbon, hydrogen, nitrogen, and sulfur as well as proximate analysis. Results of these analyses are given in Table 7-7.

The data indicates a loss in Fischer Assay oil yield during the 3-year period even though the samples had been stored under an inert atmosphere.

Table 7-8 gives a comparison of the elemental analyses of the six oil shale samples as-received. The six shales appear to be similar in elemental content with only a few exceptions; for example, the nickel content of the Kentucky shale and the barium, cadmium, vanadium and zinc content of the Ohio shale.

Table 7-2. SAMPLE DATA -- INDIANA

State:	Indiana
Sampling Date:	Unknown, DOE Oil Shale Sample Bank Sample
Amount:	6 tons
Shale:	New Albany, DOE Oil Shale Sample Bank, Reference E-88
Member:	Clegg Creek
Age:	Devonian
County:	Clark
Quadrangle:	Unknown
Type of Sample:	Outcrop

Location: Reference shale E-88 was taken from the top of an exposure of New Albany shale located on the Donald McRae farm in Clark County, Indiana. The site is approximately 25 miles north of the Ohio River at Louisville, Kentucky. The McRae farm is located on Beagle Club Road, approximately 2 miles east of Indiana Route (31). Beagle Club Road is located approximately 1 mile south of the town of Underwood, Indiana.

References:

1. Hasenmueller, N. R., "Resource Assessment of the New Albany Shale (Devonian-Mississippian) in southeastern Indiana-Preliminary Report," in Proceedings for the 1981 Eastern Oil Shale Symposium, pp. 173-180, Lexington, Kentucky.
2. Hasenmueller, N. R. and Bassett, J. L., "Stratigraphy" in N.R. Hasenmueller, and G.S. Woodard, Eds., Studies of the New Albany Shale (Devonian and Mississippian) and Equivalent Strata in Indiana, Indiana Geological Survey, for U.S. DOE/METC/05204-1128, pp. 5-32.

Table 7-8. COMPARATIVE ELEMENTAL ANALYSES PROGRAM FOR AS-RECEIVED OIL SHALE SAMPLES

Element	Oil Shale Source					
	Alabama	Tennessee	Kentucky	Indiana	Ohio	Michigan
	ppm (%)					
Ag ^b	1.1	1.3	0.13	1.6	2.2	1.0
Al	(3.37)	(3.70)	(4.86)	(4.91)	(5.47)	(4.86)
As	129	122	130	170	150	86
B	<2	<2	<2	<2	<2	<2
Ba	239	256	271	344	1346	279
Be	<4	<4	<4	<4	<4	<4
Bi	<5	<5	<5	<5	<5	<5
Ca	(0.18)	(0.51)	(0.32)	(0.27)	(0.15)	(1.38)
Cd	4	<1	2	5	34	2
Ce	64	62	69	63	59	60
Co	73	38	32	20	13	18
Cr	59	81	69	91	97	72
Cu	92	71	86	126	106	72
Fe	(6.33)	(5.84)	(4.99)	(3.75)	(3.60)	(3.50)
Ga	9	13	14	13	7	14
K	(2.26)	(2.38)	(2.38)	(2.69)	(2.37)	(2.46)
La	37	36	38	42	37	34
Li	32	33	26	33	29	30
Mg	(0.47)	(0.59)	(0.67)	(0.52)	(0.61)	(0.98)
Mn	248	168	351	178	145	326
Mo	228	162	162	128	168	94
Na	(0.19)	(0.22)	(0.27)	(0.24)	(0.20)	(0.32)
Nb	13	12	13	14	15	12
Ni	250	77	2454	175	180	74
P	<(0.01)	(0.01)	<(0.01)	<(0.01)	<(0.01)	<(0.01)
Pb	51	37	82	107	46	32
Rb	106	84	111	159	169	154
Sb	11	10	6	13	24	<5
Sc	8	6	10	11	12	11
Se	<5	<5	<5	<5	<5	8
Sn	<30	<30	<30	<30	<30	<30
Sr	40	49	69	60	63	64
Ta	<10	<10	<10	<10	<10	<10
Ti	(0.32)	(0.33)	(0.32)	(0.37)	(0.37)	(0.35)
Tl	<20	<20	<20	<20	<20	<20
V	210	153	276	487	1361	119
W	11	10	<10	<10	19	<10
Y	26	22	28	31	26	21
Zn	246	155	459	734	1067	75
Zr	81	82	86	93	103	94
F ^c	720	720	490	790	540	610
Hg ^d	10	10	<5	<5	<5	<5
U ^e	45.5	28.1	25.5	19.8	15.4	7.9
LOI ^f	(25.38)	(19.65)	(20.36)	(21.00)	(18.72)	(12.32)

^a Analyses performed by Bondar-Clegg and Company, Ltd.

^b Ag-Zr: Multi-acid digestion, plasma emission spectroscopy.

^c F: Potassium hydroxide fusion, specific ion.

^d Hg: HNO₃-HCl hot extraction, cold vapor AA.

^e U: Fluometric.

^f LOI: Gravimetric, 700°C.

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Table 7-7. ANNUAL COMPARATIVE ANALYSES OF SIX OIL SHALE SAMPLES

Sample Location	Year	F.A. Oil GPT*	Analysis, %							
			C(t)	H	N	S	Volatiles	Ash	C(f)	Moisture
Alabama	1	13.0	15.30	1.57	0.16	9.80	15.24	74.86	9.08	0.82
Alabama	2	11.9	14.80	1.76	0.48	7.75	15.66	73.86	9.02	1.46
Alabama	3	12.1	15.46	1.77	0.55	8.60	15.82	73.85	9.28	1.05
Tennessee	1	10.1	11.20	1.51	0.40	6.83	13.67	79.26	5.58	1.48
Tennessee	2	9.2	10.91	1.47	0.36	6.85	14.04	78.84	5.77	1.35
Tennessee	3	8.7	10.91	1.54	0.58	7.03	14.15	78.21	5.88	1.76
Kentucky	1	14.2	13.25	1.45	0.47	5.48	15.18	77.96	5.94	1.37
Kentucky	2	12.6	12.66	1.64	0.45	4.81	15.56	78.03	4.87	1.54
Kentucky	3	12.7	12.82	1.72	0.59	5.02	15.56	77.74	5.15	1.55
Indiana	1	15.8	13.90	1.62	0.43	2.87	13.66	77.46	6.13	2.75
Indiana	2	14.3	13.14	1.79	0.49	3.13	14.41	77.54	6.15	1.87
Indiana	3	12.0	13.32	1.80	0.59	3.20	14.55	77.73	6.04	1.68
Ohio	1	8.1	10.89	1.31	0.34	3.00	12.55	79.22	5.23	3.00
Ohio	2	9.1	10.36	1.68	0.46	2.29	12.90	79.05	5.36	2.70
Ohio	3	7.5	10.15	1.79	0.49	2.23	12.95	77.99	5.49	3.57
Michigan	1	8.2	8.15	1.99	0.24	3.10	11.58	84.27	2.60	1.55
Michigan	2	7.7	7.61	1.15	0.28	2.95	11.91	84.37	2.11	1.61
Michigan	3	7.5	7.51	1.25	0.34	2.89	11.91	83.69	2.35	2.05

* Average of 3 Fischer Assays.

C(t) = total carbon.

C(f) = fixed carbon.

settle in 55 gallon (0.2 m^3) drums. The column cell tails exited the cell around the periphery of the sparger; however, by adjusting the height of the tailings standpipe, the pulp-froth interface could be controlled at any desired level. Compressed air was metered into the bottom of each cell through a 50 μm fritted glass sparger at the rate of about 30 SLPM.

The three-pass stirred ball mill discharge, at about 40% solids, was diluted to about 5% solids with Tuscaloosa tap water containing sufficient frother, Dowfroth 250, to yield a flotation feed slurry of about 60 ppm. The flotation feed was pumped into the froth interface at a rate of about 1 pound (0.45 kg) of solids/minute/cell. A wash water spray was located about 1 foot (0.305 m) down into the top of the froth column to obtain additional cleaning of the froth. The column cell tailings products were combined and sent to one of a series of large tanks for settling and collection of the solids.

During the early stages of the column cell flotation campaign a number of variables were evaluated in an effort to optimize the production of kerogen concentrates containing between 30 and 35 gallons of oil per ton (125 and 146 L/metric ton) by Fischer Assay. During the course of these studies it was determined that, while such concentrates could be produced, high kerogen losses were occurring in the flotation tails which would preclude the production of 1,200 pounds (544 kg) of concentrate. As a result, a decision was made to produce a concentrate product having greater than 30 gallons of oil/ton (125 L/metric ton) by Fischer Assay and to retain the cell tails for recycling to the column cells for the production of a scavenger concentrate. This scavenger concentrate was then reground in the stirred ball mill for liberation of the kerogen and subsequent re-flotation.

Concentrate Preparation

The scavenger concentrate was combined with the primary concentrate and the thickened bulk concentrate was thoroughly blended in a large tank using a heavy duty mixer. The bulk concentrate was pressure filtered and oven dried at about 65°C . After drying, the concentrate was crushed and screened at 100 mesh to produce a fine sized feed suitable for hydroretorting studies. Figure 7-1 presents a flowsheet of the above described process.

Essentially all of the individual processing steps shown in Figure 7-1 was conducted in batch modes. Equipment constraints precluded the use of recycled water during the flotation production run. One thousand and fifty pounds (476 kg) of concentrate was subsequently produced and shipped to IGT in five 55-gallon (0.2 m^3) drums on June 22, 1989.

Discussion of Results and Observations

Two representative samples of the concentrate were taken for Fischer Assay; one sample represented the feed to the filter prior to drying and crushing. The second sample was taken after crushing the dried sample to pass 100 mesh. Comparison of the Fischer Assay oil yield from the two samples indicated significant differences; data from the Fischer Assays were compared and the results are shown in Table 7-9.

These data indicate that there was a 50% difference in water generated during Fischer Assay as well as a 40% increase in gas plus loss between the

Table 7-7. ANNUAL COMPARATIVE ANALYSES OF SIX OIL SHALE SAMPLES

Sample Location	Year	F.A. Oil GPT*	Analysis, %							
			C(t)	H	N	S	Volatiles	Ash	C(f)	Moisture
Alabama	1	13.0	15.30	1.57	0.16	9.80	15.24	74.86	9.08	0.82
Alabama	2	11.9	14.80	1.76	0.48	7.75	15.66	73.86	9.02	1.46
Alabama	3	12.1	15.46	1.77	0.55	8.60	15.82	73.85	9.28	1.05
Tennessee	1	10.1	11.20	1.51	0.40	6.83	13.67	79.26	5.58	1.48
Tennessee	2	9.2	10.91	1.47	0.36	6.85	14.04	78.84	5.77	1.35
Tennessee	3	8.7	10.91	1.54	0.58	7.03	14.15	78.21	5.88	1.76
Kentucky	1	14.2	13.25	1.45	0.47	5.48	15.18	77.96	5.94	1.37
Kentucky	2	12.6	12.66	1.64	0.45	4.81	15.56	78.03	4.87	1.54
Kentucky	3	12.7	12.82	1.72	0.59	5.02	15.56	77.74	5.15	1.55
Indiana	1	15.8	13.90	1.62	0.43	2.87	13.66	77.46	6.13	2.75
Indiana	2	14.3	13.14	1.79	0.49	3.13	14.41	77.54	6.15	1.87
Indiana	3	12.0	13.32	1.80	0.59	3.20	14.55	77.73	6.04	1.68
Ohio	1	8.1	10.89	1.31	0.34	3.00	12.55	79.22	5.23	3.00
Ohio	2	9.1	10.36	1.68	0.46	2.29	12.90	79.05	5.36	2.70
Ohio	3	7.5	10.15	1.79	0.49	2.23	12.95	77.99	5.49	3.57
Michigan	1	8.2	8.15	1.99	0.24	3.10	11.58	84.27	2.60	1.55
Michigan	2	7.7	7.61	1.15	0.28	2.95	11.91	84.37	2.11	1.61
Michigan	3	7.5	7.51	1.25	0.34	2.89	11.91	83.69	2.35	2.05

* Average of 3 Fischer Assays.

C(t) = total carbon.

C(f) = fixed carbon.

Table 7-9. FISCHER ASSAY RESULTS OF TWO SAMPLES OF CONCENTRATE

Sample Number	Oil		Water		Spent Shale, %	Gas Plus Loss, %
	%	GPT	%	GPT		
Filter Feed	12.1	30.4	3.6	8.6	81.8	2.5
As-Shipped	11.0	27.7	5.4	12.9	80.1	3.5

filter feed sample and the as-shipped sample. While a possible explanation of these differences might be oxidation of the kerogen, no additional analyses were made of the samples. The two Fischer Assay results were averaged to yield the results shown in Table 7-10.

Table 7-10. ANALYSIS OF BULK INDIANA CONCENTRATE

Component, wt %	
Moisture Content	1.78
Volatiles	24.44
Ash	60.82
Element, wt % (dry basis)	
Carbon	26.86
Hydrogen	3.15
Nitrogen	0.90
Sulfur	2.59
F.A.* , GPT	29.1

* Average of two Fischer Assays.

Table 7-11 shows a metallurgical balance of the column cell flotation production run. The data indicate low oil recovery; however, this low oil recovery, as well as the Fischer Assay of the flotation concentrate, are both the result of lack of effective liberation of the kerogen from a flotation feed ground to a d_{90} of 15 μm .

During pilot plant operations of the stirred ball mill grinding of the Indiana oil shale, it was noted that large volumes of gas were being liberated from the raw shale during each of the three passes through the mill. This was observed while 55-gallon (0.2 m^3) drums were used to retain the stirred ball mill discharge. The drums were filled with stirred ball mill discharge leaving about 10% of the volume as free board to facilitate moving the drums without spilling the contents. As the drums were filled and set aside it was noticed that the volume of the ground shale slurry had increased to the point that the slurry was about to overflow the drums. Subsequent stirring of the ground slurry with a heavy duty mixer was sufficient to reduce the slurry volume back to the original filling level; however, it became necessary to carefully monitor the slurry in the drums and to utilize the mixer as required after recycling the slurry to the stirred ball mill.

Figure 7-1. FLOWSHEET OF PROCESS UTILIZED TO PRODUCE INDIANA OIL SHALE FLOTATION CONCENTRATE FOR HYDRORETORTING STUDIES

No effort was made to collect samples of the gas for analysis or to accurately determine the evolved gas volume; however, a rough approximation of gas volume in one drum after 3 passes through the stirred ball mill indicated that about 2 cubic feet (56.6 L) of gas was expelled from the drum after a thorough stirring with the mixer.

The identification of significant volumes of gas evolution, as well as potential gas volatility, generated during fine grinding of Eastern oil shale should allow processors to be mindful of minimum safety standards by utilizing explosion proof motors in the fine grinding of shale. The potential for recovering and utilizing the gas as a supplemental fuel by discharging the stirred ball mill product into a stirred vessel, under negative pressure, prior to sending the ground product to flotation also is a possibility.

An additional example of gas generated by fine grinding of an Alabama oil shale was demonstrated earlier in the program. Several 55-gallon (0.2 m³) drums of shale were ground in a 120 liter Netzsch mill owned by a local coal operator. The drums were refilled with the shale slurry and sealed at the site for transportation to the Mineral Resources Institute. Within a distance of 15 miles (24 km) that the truck had transported the slurry several drums had ruptured the sealed tops and overflowed onto the truck bed. Other drum tops, while not ruptured, were bent so severely as to preclude future usage.

Reference

Schultz, C. W., Bates, J. B. and Lamont, W. E., 1989. "Column Flotation of Eastern Oil Shales". Presented at the Eastern Oil Shale Symposium, Lexington, Kentucky, November 14-17, 1989.

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Figure 7-1. FLOWSHEET OF PROCESS UTILIZED TO PRODUCE INDIANA OIL SHALE FLOTATION CONCENTRATE FOR HYDRORETORTING STUDIES

**APPENDIX A. Physical Properties and Elemental Analysis
of Indiana New Albany Shale**

**APPENDIX A. Physical Properties and Elemental Analysis
of Indiana New Albany Shale**

CALCULATIONS FOR THE 150-ton/day UNIT

Calculations for a 150 ton/day (136 metric ton/day) PFH retorting unit were conducted using the modified computer program. The given calculation conditions were as follows:

- a. Feed shale type: Indiana New Albany
- b. Capacity: 12,500 lb/h (5670 kg/h) raw shale with 6% [750 lb/h (340 kg/h)] moisture
- c. Major Properties of the shale:

- Contents:

	<u>Carbon</u>	<u>Hydrogen</u>	<u>Sulfur</u>	<u>Nitrogen</u>
	wt %			
Raw	12.37	1.14	4.67	0.45
Spent	2.46	0.12	2.77	0.09

- Density (lb/ft³): Raw shale -- 79.3 (1270.3 kg/m³)
Spent shale -- 66.0 (1057.2 kg/m³)
 - Shale particle size: -1/8 inch (-3.2 mm)
 - Overall heat of reaction for dry raw shale: -51 Btu/lb (-118 kJ/kg)
- d. Mass flux of raw shale in retort zone: 6000 lb/h-ft² (2.93 X 10⁴ kg/h-m²)
 - e. Composition of recycle gas: 90% hydrogen
 - f. Quantities and compositions of gas and oil products from retorting are given based on the data used for the moving-bed simulation.

The parameter ranges of the calculation were given by:

- a. Zone temperatures, °F:
 - Preheating: 400 to 700 (204° to 371°C)
 - Retorting: 900 to 1100 (482° to 593°C)
 - Cooling: 500 to 700 (260° to 371°C)
- b. Inlet gas to cooling zone, °F: 100 and 150 (38° and 66°C)
- c. Pressure, psig: 400, 600, 800 (2.8, 4.2, and 5.6 MPa)
- d. Residence time (in each zone), min: 5, 10, 20

Based on the basic temperature selection, the effects of different parameters on mass and energy balances, and dimensions of each zone, have been calculated. Because chemical reaction, heat and mass transfer and flow dynamics in the process are not considered in the present simulation, and

experimental data are not available yet, the effect of temperature on the retorting process is only for mass and energy balances, while pressure only affects gas densities and fluidization velocities. Similarly, the residence time affects only the height of each zone.

Typical results from the calculations for Schemes A and B are shown in Figures B-1 and B-2, respectively. All major parameters of each stream, such as temperature and mass flow rate, are presented. Gas velocity, residence time of shale, diameter and height of each zone are also listed. The ratio of recycle gas/retorting products in the retort zone, the saturation temperature, and mole fraction of water vapor in the output recycle gas from the preheating zone are also indicated.

CALCULATIONS FOR THE 150-ton/day UNIT

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- Contents:

	<u>Carbon</u>	<u>Hydrogen</u>	<u>Sulfur</u>	<u>Nitrogen</u>
	wt %			
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Based on the basic temperature selection, the effects of different parameters on mass and energy balances, and dimensions of each zone, have been calculated. Because chemical reaction, heat and mass transfer and flow dynamics in the process are not considered in the present simulation, and

DATE: 12/09/88
RUN: PFHINB02

Figure B-2. TYPICAL OUTPUT FROM PFH PROCESS COMPUTER PROGRAM: SCHEME B

IV-B-6

END

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