RETORTED OIL SHALE DISPOSAL RESEARCH

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SUMMARY

Although the retorted, or processed, shale represents the largest by-product from oil shale retorting operations, results from detailed studies indicate that it can be managed in an environmentally acceptable manner. Laboratory and field tests have demonstrated the following properties: compaction to 1600 kg/m^3, using normal vehicular traffic; cementation strength to 1480 kPa, using only retorted shale and optimum water; permeabilities as low as 1×10^{-7} cm/s, using proper handling techniques. In addition, tests have shown that dusting, auto-ignition, and leaching pose no special problems. These research results indicate that properly managed retorted shale exhibits the properties of a low-grade cement. Thermal reactions occurring during retorting and the chemical composition of retorted shale are related to the cement-like physical properties.

INTRODUCTION

In the quest for alternate energy sources, oil shale appears particularly attractive because of the large domestic deposits and because the retorting process produces liquid and gaseous fuels directly. However, the retorting process also produces large quantities of retorted shale which could pose a potentially adverse environmental impact if not disposed of properly. A mature, million-barrel-per-day oil shale industry would produce over 125 million Mg of retorted shale during each day of operation.

During the Paraho operations at the U. S. Department of Energy Anvil Points Oil Shale Research Facility, the potential problem of retorted shale disposal was recognized. A seven-stage retorted shale research program, jointly supported by the U. S. Bureau of Mines, was carried out using both laboratory and field studies (Holtz, 1976). Highlights of this retorted shale research program showed that retorted oil shale, produced by the Paraho process, can be effectively compacted and handled to produce strong and water impervious structures (Heistand and Holtz, 1980). These desirable properties of Paraho retorted shale are believed due to the formation of a low-grade cement by thermal reactions which occur during retorting.

In this paper, the chemistry of Paraho retorted shale, the nature of the thermo-chemical reactions that can contribute to its cement-like properties, and the chemistry of the leachates obtained from permeability studies will be presented. Although civil engineering information now exists which permits the disposal of retorted shale in an environmentally acceptable manner, a better understanding of the thermal reactions of retorting and the chemical composition of retorted shale may suggest changes in retorting operations which would further lessen any possibly adverse environmental impact.

EXPERIMENT DESIGN

Because the disposal of retorted shale is, ultimately, a field exercise, this paper will discuss the experimental design (and data) from field studies which have been carried out. Laboratory experimentation and data will be used to complement the results of field studies. Two field studies were carried out during the Paraho research operations. These retorted shale field studies included compaction studies and permeability, or infiltration, studies.

The field compaction studies were carried out in a relatively flat area, 2-3 km from the retorting operations (see Fig. 1). The compaction site, measuring 55 m wide by 120 m long, was divided into two sections. In one section the retorted shale was placed dry; in the other, optimum water was added before placement. The material was hauled directly from the retorted shale disposal system and spread as soon as possible. No problems with dusting or auto-ignition were noted. The material was spread in 20-30 cm layers and subjected to various compactive efforts. Approximately 12000 m^3 (15000 Mg) of retorted shale was used in these field compaction studies.

The field infiltration studies were carried out near the retorting operations. Two shallow ponds were constructed using techniques developed during the earlier field compaction studies (see Fig. 2). Both ponds were constructed out of Paraho retorted shale placed in layers to an overall thickness about 1 m. Both ponds had sloping sidewalls to obviate wall effects and to eliminate any wall-bottom interface. One pond was constructed with dry retorted shale using light compaction. The other pond was constructed of retorted shale, mixed with optimum water, and placed using heavy compaction. After construction, both ponds were filled with water and the infiltration rates were measured using staff gauges and flows through the drain lines.

RESULTS AND DISCUSSION

Compaction. The field compaction studies confirmed earlier laboratory studies regarding the effect of compactive effort, moisture addition, and aging on density and strength. Shown in Figure 3 is the relationship of compactive effort and added moisture on the densities of retorted shale. At least three in-place density measurements were made in each layer. Results show that densities averaging 1500 kg/m^3 can be achieved. The strength of the compacted retorted shale was measured using

unconfined compression (ASTM 1976). The relationship between this strength data and added moisture at various seasoning times are shown in Figure 4. The remarkable strength increase obtained with the addition of optimum water indicates the occurrence of some sort of cementing reaction. Further evidence of this cementing reaction is apparent where the compressive strength gains with aging. Aging 60 days after the addition of optimum water produced compressive strengths of nearly 1500 kPa.

Infiltration. Infiltration data for the two ponds are listed in Table 1. Also listed are in-place and core densities, moisture contents, and compressive strengths. These data show that Pond I (high compaction, optimum water) was well-constructed. Densities matched those achieved in earlier laboratory and field compaction tests. The strength, measured in a core sample (1480 kPa), exceeded those achieved during those earlier tests. The field permeability, as measured by staff gauge, (4×10^{-6} cm/s), when corrected for initial absorption and normal evaporation, approaches the value obtained from analysis of the core (6×10^{-7} cm/s). Actual infiltration from the highly compacted pond shows the permeation rate to be 3×10^{-7} cm/s.

Pond II, receiving only light compaction and no added water, showed a permeability rate of 2×10^{-4} cm/s. Although the permeability of this material is quite high, effluents could be contained in a disposal area using properly-placed, well-constructed material such as used in Pond I. Even though the loosely compacted Pond I exhibited a high permeability rate, an additional field experiment indicated that permeability may not pose a serious problem. After Pond II (light compaction) had dried thoroughly for several months following the field infiltration test, a special test was conducted. The surface was sprayed with 17,400 ℓ of water to represent a rainfall of 5 cm in 30 minutes. No effluent occurred for nearly one full day. A small seepage began the second day and continued for two days. Only 7 ℓ

were collected from the drain pipe. Essentially all of the simulated rainfall was lost to absorption and subsequent evaporation. This indicates that leaching and permeability may not be a problem for Paraho retorted shale, even when lightly compacted, because even heavy rainfall will not penetrate the pile to significant depths.

Chemical and Physical Properties. Paraho retorted shale is described according to standard soils classification as a silty-gravelly material (Holt, 1976). A size distribution diagram is presented in Figure 5. Some of the favorable properties of the retorted shale is attributed to this size distribution - like a good aggregate mix, this material has the proper ratio of fines to larger sized pieces so that the voids between the larger pieces are filled with fines. This relationship increases density, promotes strength, and reduces dusting and erosion. The chemical composition of retorted shale depends on the composition of the raw shale and the retorting process. The mineral composition of the Green River shale used in the Paraho operations consists of a complex mixture of minerals. These include: carbonates (50%), clays (40%), quartz (8%), and sulfides and others (2%). The principal carbonate mineral undergoing thermal reactions during the normal retort conditions are dolomite ($CaCO_3 \cdot MgCO_3$), or more properly ferroan ($CaCO_3 \cdot Fe_x$, $Mg_{1-x}CO_3$) where a portion of the magnesium is replaced by iron. It is believed that ferroan undergoes the following chemical reaction during normal retorting conditions:

(1) Ferroan + Heat $\rightarrow$ Calcite ($CaCO_3$) + Magnesia (MgO) + FeO + CO_2

The mean chemical analysis of Paraho retorted shale is presented in Table 2. Although it is important to know this chemical composition, it is not helpful in assessing the components responsible for the cement-like properties. Much emphasis has been placed upon the formation of reactive oxides, such as

free lime and magnesia, from carbonate decomposition. Although free lime can be formed under laboratory conditions (Heistand, Jones, Morriss, 1978), it has not been detected in the retorted shale used in the field studies. Although free lime was not detected, magnesia (MgO) has been found in Paraho retorted shale. Sulfur minerals, known to exhibit cement-like properties, have been found in Paraho retorted shale (Holt 1976). These include: anhydrite ($CaSO_4$), bassanite ($CaSO_4 \cdot 0.5H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$). These sulfur minerals present in the retorted shale may be there as a result of the raw shale composition or as a result of absorption of hydrogen sulfide by the retorted shale. It is believed that the magnesia and sulfur minerals are responsible for the cement-like properties of the Paraho retorted shale.

Many studies have been carried out concerning the analysis of leachates from retorted shale. Results from these studies are highly dependent upon the procedure that is employed. Listed in Table 3 are some of the leachate data obtained during the retorted shale studies. The data show the variations obtained from various test procedures. For the most part, the leachate consists of the major components in retorted shale (see Table 2). As the compaction is increased, the column experiments show that the leachate concentration is increased, but the total amount leached is decreased. Also, the leaching diminishes as the leachate is recirculated which would indicate that leaching should not proceed to great depths in a retorted shale disposal area. Batch experiments indicate that about 1 wt% of material is extracted from the retorted shale; this meets established engineering standards (Holtz, 1976). Data shown in Table 3 consists of materials which can contribute to salinity, toxic elements had not been considered. More recently, the U. S. Environmental Protection Agency has proposed an extraction procedure to determine hazardous wastes (EPA, 1979). Results obtained using the proposed EPA extraction procedure are shown in Table 4 for both Paraho raw and retorted shales. The low

concentrations shown in Table 4 indicate that these materials are not hazardous wastes as indicated by the U. S. EPA. These low concentrations of toxic materials found in leachates from Paraho retorted shale using the proposed U. S. EPA extraction procedure would not be increased to hazardous levels if all of these materials present in the retorted shale (see Table 2) were solubilized.

CONCLUSIONS

Detailed laboratory and field studies have shown that Paraho retorted shale can be compacted easily; is not subject to dusting, erosion, or auto-ignition; and can be handled to create structures of very low permeability. A basis for these beneficial properties can be found, in part, by an examination of the chemical and physical properties of the retorted shale. However, more studies are needed to further define these chemical and physical properties. Results from these additional studies can further reduce the possibility of any potentially adverse impact from retorted shale disposal.

ACKNOWLEDGEMENT

The retorted shale research studies discussed in this paper were carried out at the U. S. Department of Energy Anvil Points Research Facility located on the Naval Oil Shale Reserves Nos. 1 and 3 near Rifle, Colorado.

REFERENCES

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Holtz, W. G., "Disposal of Retorted Shale from the Paraho Oil Shale Project", (J0255004, U. S. Department of Interior, Bureau of Mines), Dec. 1, 1976.

U.S. EPA, "Hazardous Waste Guidelines and Regulations", Federal Register, 43, 58956-7 (1978).

TABLE 1

FIELD INFILTRATION ANALYSIS

	Pond 1		Pond 2
	Initial	Cores	Initial
Moisture, wt%	22.1	18.5	0.0
Density, Bottom kg/m^3	1488	1697	1466
Side kg/m^3	1395		
Strength, kPa		1482	
Permeability, cm/sec x 10^{-6}	0.3	0.6	2000

TABLE 2

RETORTED SHALE COMPOSITION

A. Major Elements

Element	Wt%	Element	Wt%
Al	4.6	Mg	4.3
Ca	12.6	Na	2.0
Fe	2.3	Si	17.3
K	1.4	Ti	0.2

B. Trace Elements

Element	ppm	Element	ppm
As	62	Mo	35
B	140	Ni	35
Ba	530	Pb	33
Cd	1	Sb	3
Cr	38	Se	2
Cu	51	Sn	< 2
Hg	0.02	V	108
		Zn	83

TABLE 3

FIELD LEACHATES

Material	Loose Fill	Compacted
Leachate Volume, ℓ	250,000	1500
pH	10.4	11.4
	mg/ℓ	mg/ℓ
Calcium	480	55
Magnesium	2.6	1.4
Sodium	1,740	3510
Potassium	161	91
Silicon	3	3.3
Sulfate	1,112	1314
Chloride	651	112
Alkalinity (as $CaCO_3$)	1.9	454
Arsenic	5.8	3.9
Boron	1.7	1.7
Cadmium	< 0.005	< 0.005
Lead	0.07	0.07
Mercury	0.012	0.010
Molybdenum	1.7	4.3

TABLE 4

LEACHATE DATA
EPA EP TEST (RCRA)

Arsenic	< 0.1	ppm
Barium	< 10	ppm
Cadmium	< 0.05	ppm
Chromium	< 1	ppm
Mercury	14	ppb
Lead	220	ppb
Selenium	23	ppb
Silver	30	ppb

FIGURE 1

FIELD COMPACTION SITE

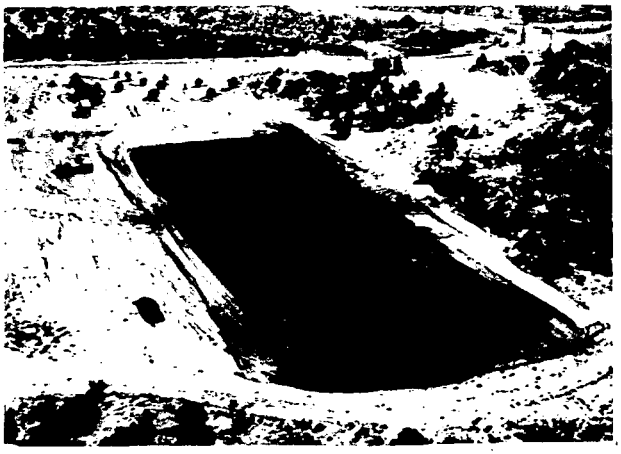

FIGURE 2

FIELD INFILTRATION SITE

POND 2 POND 1

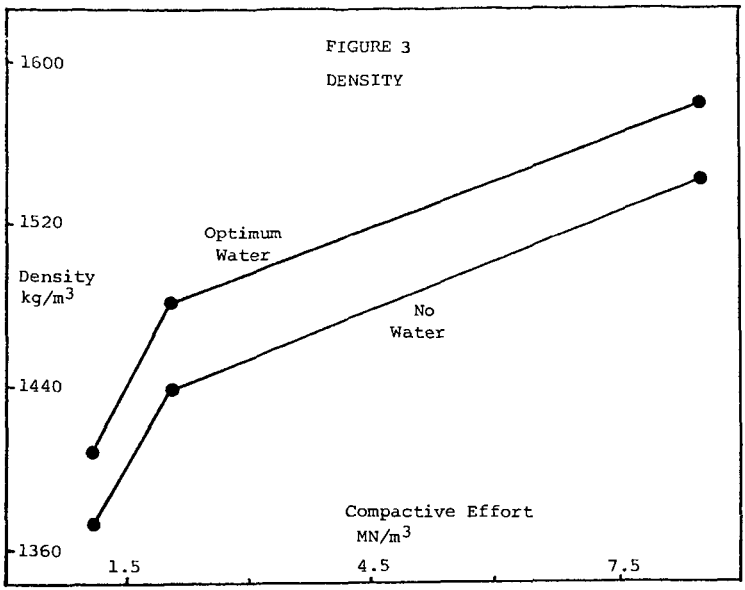
FIGURE 3
DENSITY
1600
1520
1440
1360
Density
kg/m3
Optimum
Water
No
Water
Compactive Effort
MN/m3
1.5
4.5
7.5

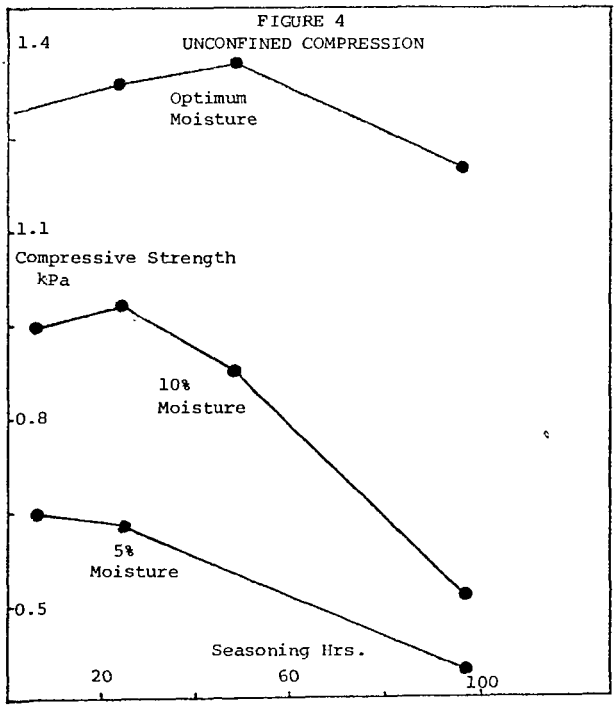
FIGURE 4
UNCONFINED COMPRESSION
1.4
Optimum
Moisture
1.1
Compressive Strength
kPa
10%
Moisture
0.8
5%
Moisture
0.5
Seasoning Hrs.
20
60
100
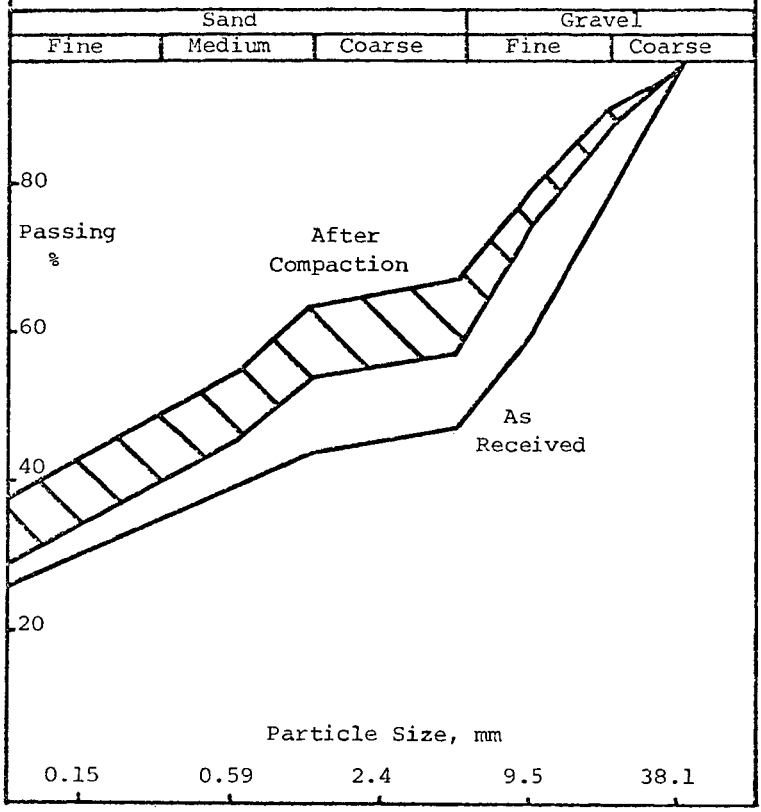
FIGURE 5
GRADATION RESULTS