Spent Shale Grouting of Abandoned In-Situ Oil Shale Retorts

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In vertical modified in-situ (VMIS) oil shale retorting, the resource is processed in the ground. Large chambers of rubblized oil shale are formed by mining out about 20 to 40 percent of the in-place shale and blasting the balance into the created void. The mined-out material is brought to the surface and oil is recovered from it by surface retorting. The in-place material is pyrolyzed to recover oil, leaving large numbers of abandoned retort chambers underground.

This type of oil shale processing may result in a number of environmental problems including in-situ leaching of the abandoned retorts, low resource recovery (large pillars are required to support the overburden), and subsidence. These problems may be mitigated by filling abandoned retorts with a grout prepared from spent shale produced during surface retorting of the mined shale. This would fill the void space created by mining, thus improving retort structural strength and stiffness, and reduce retort permeability to groundwater flow. If sufficient strength could be developed, it may be possible to design retorts so that the pillars could be retorted and resource recovery improved.

This paper summarizes the results of laboratory investigations to produce a grout from spent shale. Spent shale grouts may be variously produced by modifying surface retorting conditions and/or by adding chemicals such as limestone or gypsum to the spent shale. A number of processes have been proposed and investigated including heating in steam at 700°C, limestone addition to surface spent shale followed by calcining at 1000°C, and limestone addition to raw shale followed by calcining at 1400-1500°C. This paper reviews these data in the framework of required grout characteristics for effective environmental control and technical and economic feasibility.

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2. RETORT ABANDONMENT ENVIRONMENTAL ISSUES

Figure 1 shows in simplified form the relative positions of the target oil shale layer, the Mahogany Zone, fractured oil shale artesian aquifers, and VMIS retorts and summarizes the resulting environmental problems—contamination of surface and ground waters by leaching of in-situ spent shales and mixing of lower and upper aquifer waters, overburden cracking and ground subsidence, and low resource recovery.

The VMIS process requires a thick, continuous, vertical section of oil shale not interrupted by significant thicknesses of barren rock (Smith, 1978). Based on commercial designs of industrial developers, it is apparent that about 300 feet of continuous vertical oil shale is required for the process to be economical. Most of the resources where necessary geologic conditions exist are in the Piceance Creek Basin of Colorado where confined aquifers penetrate the oil-bearing strata (Weeks et al., 1974). In most of this region, the Mahogany Zone, which is the target of VMIS retorting, is 100 to 200 feet thick. In order to have a sufficiently long vertical section of oil shale, the installed retorts must intersect the stratum immediately above and/or below the Mahogany Zone where water-bearing zones exist. Therefore, it will be difficult to locate VMIS retorts in completely dry zones and a geometry similar to that shown in Figure 1 will be used.

This manner of locating retorts will create the potential for water to flow from one aquifer to the other through the retorts. During development and retorting, aquifers will be dewatered. Following abandonment, groundwater will re-invade the aquifers and fill the retorts, leaching spent shale. The leached material, which includes many organic and inorganic compounds, can be transported in the aquifers and ultimately discharged into streams and springs or withdrawn from wells. Local streams which receive groundwater inflow are tributary to the Colorado River system where salinity is already of national and international concern.

If a retort penetrates one aquifer, there will be a hydraulic gradient in the horizontal direction across the retort causing horizontal flow through the retort which will transport leached material into the aquifer. If a retort penetrates more than one aquifer and the aquifers are at different heads, there will also be a vertical hydraulic gradient causing flow through the retort from one aquifer to the other. This condition could be more serious as the vertical gradient resulting from this condition could be greater than the horizontal gradient; thus the rate of flow through and leachate transport away from the retort would be greater.

The problem of aquifer and eventual surface stream pollution by leaching of vertical modified in-situ retorts in the Piceance Creek Basin has been quantified by Fox (1979). This study concluded that it could take centuries before significant groundwater degradation would occur, due to the low flow velocities in many areas of the Basin. However, the report pointed out that the potential long-term effects could be serious due to the critical issue of salinity in the Colorado River system and the slow self-purification properties of groundwater aquifers. Leachates could result in salinity increases in the Colorado River at Lees Ferry of from 0.03 to 50 mg/l (Fox, 1979). A TDS increase of 50 mg/l in the Colorado River would have a significant
Subsiding ground surface

Ground surface

Piezometric surface

Gaining reach of stream

Upper Aquifer

Mahogany Zone

Lower Aquifer

Abandoned retorts

Pillars
economic impact upon irrigated agriculture. Kleinman (1974) estimates the total economic loss due to Colorado River salinity increases to be $200,000 to $400,000 per year per mg/l (1974 dollars). Additionally, elevated concentrations of certain toxic or carcinogenic organic materials may occur in aquifers or surface streams. If these waters were used for municipal supply or stock water, local health problems might result.

In some areas of the Piceance Creek Basin, such as lease tract C-b, water quality of the lower aquifer is much worse than that of the upper aquifer. In these cases, contact between the two aquifers created by the retorts would permit degradation of the upper aquifer in the absence of leaching.

Resource recovery in VMIS retorting is poor. Oil recovery is low and 25 to 50 percent of the developed area must be left intact as pillars between retorts to support the overburden. If sufficient strength could be developed in abandoned retorts, it might be possible to design a retorting system so that pillars could be retorted and resource recovery improved.

Finally, considerable concern exists over the long-term stability of abandoned retorts. Computational techniques are inadequate to predict incidences of subsidence, and there are presently no field data available to assess this problem. (Field experiments have consisted of single, small retorts while commercial operations may use many hundreds of very large retorts.)

3. SPENT SHALE GROUTING

The three principal environmental problems associated with VMIS retorting—contamination of surface and ground waters, subsidence, and low resource recovery—may be alleviated by filling the abandoned in-situ retorts with a grout based on surface spent shale. This grout would fill some of the voids, reducing the permeability of the retorts and provide for protection against subsidence by increasing retort stiffness and strength. If adequate strength could be developed in the retorted mass, it may be feasible to retort some of the pillars, thus improving resource recovery.

A cheap material, such as spent shale, would have to be used as the basis of such a grout because 9 to 13 ft$^3$ of voids must be filled for each barrel of oil recovered. Thus, conventional grouting materials are too costly for this application (Fox et al., 1978). The feasibility of this proposal depends on the properties of spent shale and the criteria required for the grout.

SPENT SHALE

Oil shale, which is a low-grade fossil fuel, produces about 1.4 tons of solid waste, referred to as spent shale, for each barrel of oil produced. This material typically contains 0.1 to 4 percent residual carbon, has little strength, and is easily crushed to a fine powder. The major elements in spent shales (greater than 1 percent by weight) are iron, calcium, magnesium,
potassium, silicon, aluminum, oxygen, and sodium. The major mineral phases depend upon the retorting conditions and may include carbonates for low retorting temperatures and silicates for higher temperatures.

The feasibility and methods of forming an adequate cementitious grout from spent shale depend on the chemical reactions that occur during surface retorting. Production of cementitious properties depends principally on the absence of char and the formation of calcium silicate compounds such as tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$) and dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$), which are the major active compounds in portland cement.

In the manufacture of portland cement, these calcium silicate compounds are formed from lime and silica produced by the decomposition of limestone and clay in reactions such as:

$$3\text{CaO} + \text{SiO}_2 \rightleftharpoons 3\text{CaO} \cdot \text{SiO}_2 \quad (1)$$

$$2\text{CaO} + \text{SiO}_2 \rightleftharpoons 2\text{CaO} \cdot \text{SiO}_2 \quad (2)$$

The formation of these compounds, rather than noncementitious ones such as $\text{CaO} \cdot \text{SiO}_2$, depends upon lime and silica being in near stoichiometric ratios.

Colorado oil shales contain an abundance of dolomite, quartz, and feldspar and are deficient in calcium relative to silica compared to other cement raw mixes. A number of investigations (Campbell, 1978; Campbell and Taylor, 1978; Burnham et al., 1978; Parker et al., 1978; and Heistand et al., 1978) have indicated that some free lime can be formed, char can be removed, and cementitious properties produced in spent shales.

PRODUCTION OF SPENT SHALE GROUTS

Three strategies have been proposed for manufacturing a grout from spent shale—grout production from raw shale, grout production from as-received surface spent shale, and grout production from treated surface spent shale. Each of these is summarized in Table 1 and discussed here.

Grout Production from Raw Shale

Sellers and Chapin (1959) obtained a patent on the production of portland cement from a 1.8:1 mixture of limestone and raw oil shale. The coarse-ground raw shale and limestone are ground to a powder and fired at 1400 to 1500°C to form portland cement clinker. The lime and silica content of the shale (with additional lime) are the raw materials. The high energy requirements, and hence cost, associated with this process make it economically unattractive for grouting of in-situ retorts.

Grout Production from Treated Spent Shales

A cementitious grout may also be produced from spent shale by heat treating as-received spent shale, by using admixtures such as gypsum and lime, or by changing the operating conditions of existing retorting processes, such as Lurgi or Paraho. Significant modifications in existing
<table>
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<td>Sample preparation</td>
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<td>Farris, 1979</td>
<td>Direct-mode retorting 2 hr at 822°C</td>
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<td>Mallon, 1979</td>
<td>Oil recovery at 500°C in N₂, char combustion below 650°C in N₂-air mix, temperature raised to 700°C in 100% air, then 70 min in 100% steam at 700°C</td>
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<td>Mehta and Persoff, 1980</td>
<td>1:1 mixture of Lurgi spent shale and limestone, calcined 1 hr at 1000°C, ground 5% gypsum added</td>
<td>3750 ASTM C 109, cured 28 days</td>
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<td>AS-RECEIVED SPENT SHALE</td>
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<tr>
<td>Culbertson et al., 1970</td>
<td>TOSCO</td>
<td>Compacted with 20% moisture</td>
<td>200-500</td>
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<td>Compacted at 56,000 ft-lb/ft³ (ASTM D1557)</td>
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<td>Nevens et al., 1977</td>
<td>Lurgi</td>
<td>Grout with 0.75 water-solids ratio, cured 24 days at 180°F</td>
<td>up to 200 ASTM D 2434</td>
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<td>Peterson et al., 1978</td>
<td>Indirect-heat</td>
<td>Compacted at 56,000 ft-lb/ft³</td>
<td>104</td>
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a Direct comparison of results is not possible because various test methods were used.
b Optimum retorting conditions for permeability were slightly different from optimum for strength.
processes may sacrifice oil production and result in a new, high-risk technology while modification of as-received spent shale has the advantage of using existing technology for both the retorting and subsequent heat treatment and thus, does not interfere with oil production.

Three investigations have been conducted on these types of processes. Mallon (1979) produced a low-strength grout by exploiting retorting chemistry in a bench-scale retort. Farris (1979) investigated the effects of various retorting conditions on spent shale strength, and Mehta and Persoff (1980) produced a high-strength hydraulic cement by adding limestone to Lurgi spent shale and heating the mixture at 1000°C. Each of these approaches is discussed here.

Farris (1979) operated a laboratory retort to determine retorting conditions which would maximize the strength of compacted spent shale. Direct-mode retorting for 2.0 hours at 822°C gave a strength of 270 psi. Indirect-mode retorting for 2.9 hours at 832°C gave a strength of 325 psi. The strength development was attributed to the formation of interlocking acicular crystals, thought to be hydrated calcium aluminum sulfate. These strengths were measured on samples which were compacted with 25 percent moisture to Proctor densities of 96 to 100 percent, and thus are not representative of strengths obtainable in grouted retorts.

Mallon, on the other hand, used the work of Campbell (1978) and Burnham et al. (1978) to develop a process that would produce cementitious compounds. He retorted Anvil Points oil shale in a small laboratory electric furnace. Oil recovery, char combustion, and cement formation were carried out in separate steps. Mallon first heated the shale to 500°C in nitrogen to remove the oil by pyrolysis. The char was then completely burned off by gradually introducing air while holding the temperature below 650°C to prevent the decomposition of carbonates. The gas flow was then changed to 100 percent air for 15 minutes while the temperature was raised to 700°C and then to 100 percent steam for 70 minutes at 700°C to form cementitious compounds. The resulting clinker was pulverized and slurried and poured into spent shale to simulate grouting of in-situ rubble. The grouted rubble has a 10-week compressive strength of 522 psi and a 4-week permeability of 4 x 10^-7 cm/sec.

Mehta and Persoff (1980) produced a high-strength hydraulic cement from Lurgi spent shale by heating a 1:1 mixture of limestone and spent shale for 1 hour at 1000°C. The resulting cement has a 28-day compressive strength of 3150 psi (ASTM C 109). The addition of 5 percent gypsum by weight to the cement produced a 28-day compressive strength of 3750 psi while 10 percent gypsum addition to the raw mix produced a strength of 4375 psi.

Grout Production from Untreated Surface Spent Shale

Other investigators have proposed the use of untreated spent shale to seal abandoned in-situ retorts. The developers of lease tract C-a, for example, proposed to use as-received surface spent shale with additives to backfill abandoned retorts and are presently conducting an investigation of this option under U. S. Bureau of Mines funding. In this strategy, spent shale from a surface process is slurried with water, admixtures such as slurry fluidizers are added, and the slurry is pumped into the abandoned retorts. This strategy has the advantage of being cheaper than the other two strategies, but it is presently uncertain whether it can produce sufficiently low permeabilities and adequate strength and stiffness.
Nevens et al. (1977) simulated the backfilling of an abandoned VMIS retort with a slurry of Lurgi spent shale. Unconfined compressive strengths of the set slurries ranged from 5 to 200 psi. Permeability measured by ASTM D 2434 on the Lurgi spent shale decreased from initial values of $10^{-4}$ cm/sec to $10^{-5}$ to $10^{-6}$ cm/sec after 28 days. The temperature at which spent shale is burned to provide heat for the retorting process appeared to be important. In-situ spent shale was observed to rapidly absorb water (4 gallons per cubic foot), suggesting that slurries may be dehydrated when pumped into abandoned retorts. In a test to simulate grouting of an in-situ retort, a slurry with 164 percent by weight of water was poured into a hand-packed drum of in-situ spent shale and water was drained from the bottom. No cementation was observed and the compressive strength after 13 days of curing was only 16 psi.

Rheological measurements by Persoff (1980) showed that slurries of Lurgi spent shale fit the Casson flow model; that is, they had a finite yield stress. The yield stress increased with decreasing water-solids ratio (wsr) in the grout, and ranged from 4 dyne/cm$^2$ for a slurry with wsr of 1.8 to 167 dyne/cm$^2$ for wsr of 0.8. Slurries with wsr greater than 1.0 were considered unsuitable for grouting because the suspensions were unstable and settled leaving a clear supernatant. Addition of common cement-slurry fluidizers to slurries with wsr of 1.0 changed the flow behavior to Newtonian, i.e., the yield stress was reduced to zero. A sample simulating a grouted retort was prepared by flowing grout with wsr of 0.8 and 5 percent added portland cement into pre-wetted spent shale rubble. Permeability of this specimen was $2 \times 10^{-5}$ cm/sec.

Several investigators studying the stabilization of surface spent shale disposal piles observed self-cementing properties of untreated spent shale. In all of these studies, strength and permeability were measured on samples which were compacted with near-optimum moisture content, and thus are not representative of strengths or permeability produced by in-situ grouting.

Culbertson et al. (1970) studied the stabilization of spent shale from a TOSCO retort. Shear strength and compressive strength of all samples increased gradually with time, suggesting a cementitious reaction. Compressive strengths in the range of 250 to 500 psi were obtained. Strength development was positively correlated with the amount of cohesive hydrates formed, as detected by differential scanning calorimetry. After 15 days of setting, no loss of strength was reported when samples were resaturated with water.

Peterson et al. (1978) studied the geotechnical properties of a fine-grained surface-retorted spent shale from an indirect-heating process to evaluate the stability of disposal piles. Unconfined compressive strengths of compacted samples increased with time, indicating some self-cementing properties. The maximum compressive strength developed was 104 psi; this required a compaction effort of 56,000 ft-lb/ft$^3$.

Compaction studies on spent shales from a Paraho direct-mode semiworks retort showed that unconfined compressive strengths up to 200 psi were obtained with 56,000 ft lb/ft$^3$ of compactive effort at 22 percent moisture content. Spent shale was described as a low-grade cement (Holtz, 1976). Permeability of this material was measured after compactive efforts ranging from 6,200 to 56,000 ft-lb/ft$^3$ under stresses of 50 to 200 psi.
Observed permeabilities ranged from $8 \times 10^{-8}$ cm/sec at 200 psi for maximum compactive effort, to $1.5 \times 10^{-5}$ cm/sec at 50 psi for minimum compactive effort. Despite great variability reported for the material it was considered suitable for use in earth dams.

EVALUATION

The preceding section presented several methods to produce a grout from oil shale materials. These included direct conversion of raw shale, modification of operating conditions of the surface retort, additional treatment of as-received spent shale, or addition of admixtures to as-received spent shale. The relative merits of these approaches depend on a wide range of factors including grouting criteria, cost, availability of technology and raw materials, and properties of the raw materials. There is presently inadequate information to select among the proposed methods, as additional experimental work is required to demonstrate feasibility and determine design criteria. However, it is instructive at this point to discuss potential grouting criteria and to qualitatively evaluate the various processes within this framework.

The characteristics of a grout used to seal an abandoned in-situ retort will depend on the goals of the grouting operation: alleviation of aquifer disruption, subsidence control, and/or enhanced resource recovery. The specific goals of any abandonment plan will depend on the geologic and hydrologic conditions of the specific site and societal goals regarding resource recovery. These criteria will have to be determined on a case-by-case basis. However, as a minimum, any grout used to seal an abandoned VMIS retort should have the following characteristics:

(1) The grouted area must be impermeable enough to prevent the degradation of local groundwater or surface water.

(2) The grouting material must be chemically stable in the presence of saline groundwater.

(3) The grout viscosity must be low enough and the setting time long enough for the slurry to penetrate a large area.

(4) The grouted area should be able to withstand hydrostatic and overburden pressures, depending on the application. The hydrostatic pressure is due to natural head differences that exist between the aquifers surrounding the oil shale deposits in some areas and to significant dewatering during retorting.

Preliminary structural analysis of retorts indicates that with a 45 percent extraction ratio (called for in development plans), no grouted retort strength or stiffness is required; that is, the overburden and pillars are stable as designed even if left ungrouted. Increasing resource recovery beyond 45 percent requires the substitution of grouted retorts for pillars and the development of strength and stiffness in the retorts. One hundred percent extraction can be realized if the grouted retorts have a strength of about 1000 psi and a stiffness (tangent modulus at zero strain) of 500,000 psi. This modulus requirement assumes that no retorts are left ungrouted at the end of the project, and that retorts are grouted soon after they are burned. The actual temporal sequence of retorting and grouting is important.
Brown et al. (1977) estimated that an average post-grouting permeability two orders of magnitude lower than the host rock would be required to keep the incremental salt loading to Piceance Creek less than 100 mg/l per 30,000 barrel-per-day production. The value proposed was $3 \times 10^{-6}$ cm/sec.

Based on these criteria and the previously reported work, it appears that grout production from as-received spent shales and various treated spent shales may achieve a sufficiently low permeability to minimize contamination of surface and ground waters. Nevins et al. (1977) measured a 28-day permeability of $3 \times 10^{-6}$ cm/sec for a Lurgi spent shale produced at moderate temperatures. Lurgi spent shales produced at higher and lower temperatures had higher permeabilities. These investigators observed that the permeability decreased over time, and they hypothesized that it may be possible to obtain a permeability of $10^{-7}$ cm/sec, given sufficient time. Similarly, Holtz (1976) measured permeabilities as low as $8 \times 10^{-8}$ cm/sec for compacted Paraho spent shales, and Mallon (1979) measured a permeability of $4 \times 10^{-7}$ cm/sec for a grouted sample of spent shale.

The most important factors for control of overburden cracking and subsidence are design strength of pillars and stiffness of the grouted retorts. Presumably, if the pillars are properly designed, they will provide adequate strength. No stiffness measurements have been reported for grouts studied.

Adequate strength and stiffness of grouted retorts are required for enhanced resource recovery. A compressive strength of about 1000 psi would have to be developed in the grouted retort to permit recovery of one hundred percent of the pillars. Strengths have been measured by several methods, but in most cases the samples (low moisture content, compacted) were not representative of grout in an in-situ retort. The grout proposed by Mehta and Persoff (1980) appears the most likely to satisfy the structural requirements for increased resource recovery.

These results indicate that the goals of retort abandonment and grouting criteria must be clearly defined before a grout can be selected. If in-situ leaching and subsidence are addressed, it may be possible to control these problems by filling the abandoned retort with a slurry of as-received spent shale. A small amount of fluidizer would probably be added to reduce the viscosity. The projected cost of this option is approximately $3.54 to $1.50 per barrel of oil for retorts located on lease tracts C-a and C-b (Persoff and Fox, 1980). On the other hand, enhanced resource recovery would require a relatively high-strength cement at a considerably higher cost. Economic trade-offs must be made between leaving some resource unrecovered and obtaining improved resource recovery at a greater cost.

4. SUMMARY

Vertical modified in-situ retorting may result in in-situ leaching of abandoned retorts, overburden cracking and subsidence, and low resource recovery. These problems may be controlled by filling the abandoned retorts with a grout based on surface spent shale. A number of grouts with a range of properties have been proposed. These include production of portland cement from raw shale, development of high-strength hydraulic cement by lime addition to Lurgi spent shale, development of low-strength grout by retorting in steam at 700°C following oil recovery and char combustion, and use of as-received spent shales with various additives.
These investigations suggest that untreated spent shale may be used to control in-situ leaching and subsidence. However, if additional resource recovery is required, a higher strength grout will be required.

5. REFERENCES


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