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HYDRAULIC CEMENT PREPARATION FROM LURGI SPENT SHALE

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P. K. Mehta, P. Persoff, and J. P. Fox

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P. K. Mehta
University of California
Berkeley, California 94720

P. Persoff and J. P. Fox
Energy and Environment Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

ABSTRACT

Low cost material is needed for grouting abandoned retorts. Experimental work has shown that a hydraulic cement can be produced from Lurgi spent shale by mixing it in a 1:1 weight ratio with limestone and heating one hour at 1000°C. With 5% added gypsum, strengths up to 25.8 MPa are obtained. This cement could make an economical addition up to about 10% to spent shale grout mixes, or be used in ordinary cement applications.

INTRODUCTION

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% 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 re-torted and resource recovery improved.

<u>Retort Abandonment Environmental Issues</u>

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

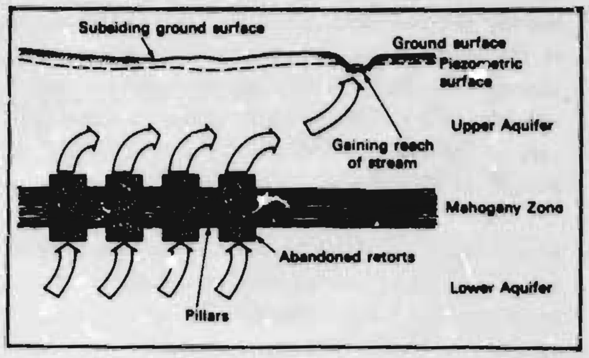

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Figure 1. Schematic of in-situ retorts and aquifers in Piceance Creek Basin, showing potential for subsidence and spent shale leaching.

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 from 90 to 210 m (300 to 700 ft) 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 30 to 60 m (100 to 200 ft) 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 result.

This manner of locating retorts will create the potential for water to flow vertically or horizontally 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 in 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.

Resource recovery in VMIS retorting is poor. Oil recovery is low and 25 to 50% 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.)

Backfilling the abandoned retorts with a grout is a possible solution to these problems. The grout would improve the strength and stiffness and reduce the permeability of the abandoned retort. The increased strength and stiffness would provide protection against subsidence. If adequate strength could be developed in the retort, it may even be feasible to extract oil from the pillars between the retorts, thus improving resource recovery. The grout would also reduce the permeability of the abandoned retort by filling the voids. This would minimize the flow of groundwater through the retorted area and thus minimize the leaching of materials from the retorted shale.

The salient feature of the retort backfilling problem is the volume of voids to be filled. Depending on the void ratio in the retorts, from 0.23 to 0.37 m^3 (8 to 13 ft^3) must be filled per barrel of oil recovered. This requires that a cheap material be used; because of the large amount of material involved, freight charges make even imported waste material, such as Wyoming fly ash, too expensive to consider. This motivates one to consider the use of surface retorted spent shale as a grout material.

Requirements for the grouted retort are permanence, low permeability and adequate strength and stiffness to satisfy structural requirements. These properties would be enhanced if the grout used contained some cementitious material. Therefore we investigated the cementitious properties of Lurgi spent shale and developed a method to enhance them.

EXPERIMENTAL

Selection and Evaluation of Raw Material

Lurgi spent shale was selected for evaluation because this process is under active consideration for application at both tracts C-a and C-b. It is also finely ground and contains little residual organic carbon which could interfere with cementing. A sample of Lurgi spent shale from experimental run 9 (1976) was obtained through the courtesy of Amoco Oil Co. (York, 1978). In this run, Colorado oil shale was retorted at 530°C and subsequently burned at 700°C. The sample we studied was collected from the electrostatic precipitator, so it represents the finest size fraction (about 33%) of spent shale from this process.

Mineralogical analysis by X-ray diffraction (XRD) showed that the minerals present in the original shale remained essentially unchanged during the retorting operation. Properties of Lurgi spent shale including the mineralogical analysis, particle size distribution, and elemental analysis by soft X-ray fluorescence are shown in Table 1.

Cementing characteristics of the shale and the hydraulic cements prepared from it were evaluated by ASTM Method C 109. According to the standard procedure, a cement-sand-water mortar in weight ratio 1:2.75:0.5 is prepared, 5-cm mortar cubes are cured in 100% humidity at room temperature, and the compressive strength of the cubes is measured. A slightly modified test procedure had to be used in that a water-cement ratio of 0.625 was needed to obtain workable mortars from mixtures of Lurgi spent shale cements and ASTM C 109 standard sand.

The Lurgi spent shale as received had too little cementing strength to measure by this method--the cubes broke upon demolding. When samples of Lurgi spent shale were heated for one hour at 800, 900, and 1000°C, and tested, none of the samples had any cementing strength. X-ray diffraction showed that no cementitious calcium compounds were present in any sample, but that large amounts of akermanite, $Ca_2MgSi_2O_7$, a non-cementing silicate, had been formed.

Addition of Limestone to Raw Mix

From the above, it was obvious that some changes had to be made in the composition of the spent shale if hydraulic cement of adequate strength was to be developed from Lurgi spent shale. A comparison between chemical analyses of Lurgi spent shale and a typical portland cement raw mix showed that for the formation of hydraulic calcareous compounds, the spent shale has excess SiO_2 and MgO and was deficient in CaO. Therefore an experimental program was planned in which $CaCO_3$ was added to Lurgi spent shale and the mixture heated. Details of the procedure are presented in Mehta and Persoff (1980).

Determination of Optimum Calcining Temperature

The first experiment was to determine the minimum temperature needed to produce hydraulic compounds in a mixture of limestone and Lurgi spent shale. A 1:1 by weight mixture was heated at 900, 950, 1000, and 1100°C. The resulting clinkers were ground to a powder, analyzed by XRD for minerals, and tested by ASTM C 109 for cementing strength. The results of these tests are shown in Table 2. These data show that with the added $CaCO_3$ (raising the CaO-SiO_2 ratio) no akermanite was formed, and β-C_2S*, an active compound of portland cement, was formed. Maximum strength was developed at 1000°C even though some undecomposed $CaCO_3$ was still present. This can be attributed to partial loss of reactivity of the cementitious compound, β-C_2S, due to crystal growth at the higher temperature of heat treatment. Further experiments were conducted at 1000°C.

Determination of Optimum Raw Mix Ratio

The next experiment was conducted to provide information on the optimum ratio of $CaCO_3$ to spent

* Abbreviated formulae used by cement chemists are: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3. Thus, for example, C_4AF = $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

Table 1. Properties of Lurgi spent shale as received.

Mineral analysis[a]		Elemental analysis,%[b]		Particle size analysis,%[c]	
Quartz	present	Na_2O	2.3	> 30.3 μm	0.6
Calcite	present	MgO	7.5	17.9-30.3 μm	2.1
Dolomite	present	Al_2O_3	7.2	10.0-17.9 μm	4.9
Feldspar	present	SiO_2	32.0	6.6-10.0 μm	9.0
Free lime	not detected	CaO	21.8	3.94-6.6 μm	25.7
		Fe_2O_3	2.7	< 3.94 μm	57.7
		Ignition loss (mainly carbonate)	20.0		

a) by X-ray diffraction.

b) by X-ray fluorescence--elements are expressed as oxides.

c) analysis supplied by Lurgi.

Table 2. Mineralogical analysis and compressive strength of cements made by one hour heat treatment of a mixture of equal parts by weight of $CaCO_3$ and spent shale.

Minerals present[a]	Temperature of heat treatment			
	900°C	950°C	1000°C	1100°C
Akermanite	N	N	N	N
C_3S	N	N	N	N
β-C_2S	W	W	M	M
C_3A	W	W	W	W
$CaCO_3$	VS	S	W	N
28-day compressive strength, MPa[b]	6.4	9.7	18.8	14.5

a) by X-ray diffraction

b) by modified ASTM C 109.

N=none W=weak M=medium S=strong VS=very strong

shale which would yield cements of good strengths when mixtures were heated at 1000°C. Weight ratios ranging from 0.5:1 to 2:1 were tested.

The results of mineralogical analyses, free CaO determination, and compressive strength tests of the cements of this series are shown in Table 3. The XRD data are also illustrated in Figure 2 for some of the mixtures. The compressive strength data indicated that for the 1000°C heat treatment, the 1:1 mixture represents the optimum composition. Under moist curing conditions at ambient temperature the cement made from this composition continued to develop strength up to the test age of 90 days which shows the long-term stability of the products of this cement in moist environments.

Figure 2 shows that the 1:1 mixture produced the greatest amounts of desired compounds, β-C_2S and C_3A, upon heating, while more $CaCO_3$ resulted in the presence of excess uncombined CaO. This extra CaO results in unsoundness of the cement, caused by delayed hydration and expansion which disrupts setting. This is reflected in lower strengths shown in Table 3. Therefore the 1:1 mixture at 1000°C produces the best cement. Further experiments were performed using this ratio and temperature.

Effect of Water Reduction and Gypsum Addition

As mentioned above, in order to obtain mortars with desired flow characteristics, it was necessary to use a higher water-cement ratio than specified by ASTM C 109. It was however possible to use a water-cement ratio which was almost equal to the one in the standard procedure when the standard ASTM C 109 sand was replaced by a coarser sand. Thus, a change in the water-cement ratio from 0.625 to 0.52 in the mortar containing the 1:1 cement composition resulted in a corresponding gain in compressive strength which increased from 17.9 to 21.7 MPa.

Table 3. Mineralogical analysis, free lime, and compressive strength of cements made by heat treatment of various proportions of $CaCO_3$ and Lurgi spent shale, 1 hr @ 1000°C.

Minerals present[a]	$CaCO_3$: spent shale ratio by weight							
	2:1	1.75:1	1.5:1	1.25:1	1:1	0.75:1	0.5:1	0:1
$CaCO_3$	VS	VS	W	W	N	N	N	N
Akermanite	N	N	N	N	N	N	M	VS
C_3S	N	N	N	N	N	N	N	N
β-C_2S	W	W	M	M	M	M	W	N
C_3A	W	W	M	M	M	M	W	N
CaO	S	S	S	S	N	N	N	N
% Free CaO[b]	12.2	9.0	7.9	6.0	3.1	1.5	0.64	0
28-day compressive strength, MPa[c]	5.8	8.3	8.3	6.1	17.9	NA	poor	nil

a) by X-ray diffraction.

b) by ASTM C 114.

c) by modified ASTM C 109.

N=none W=weak M=medium

S=strong VS=very strong

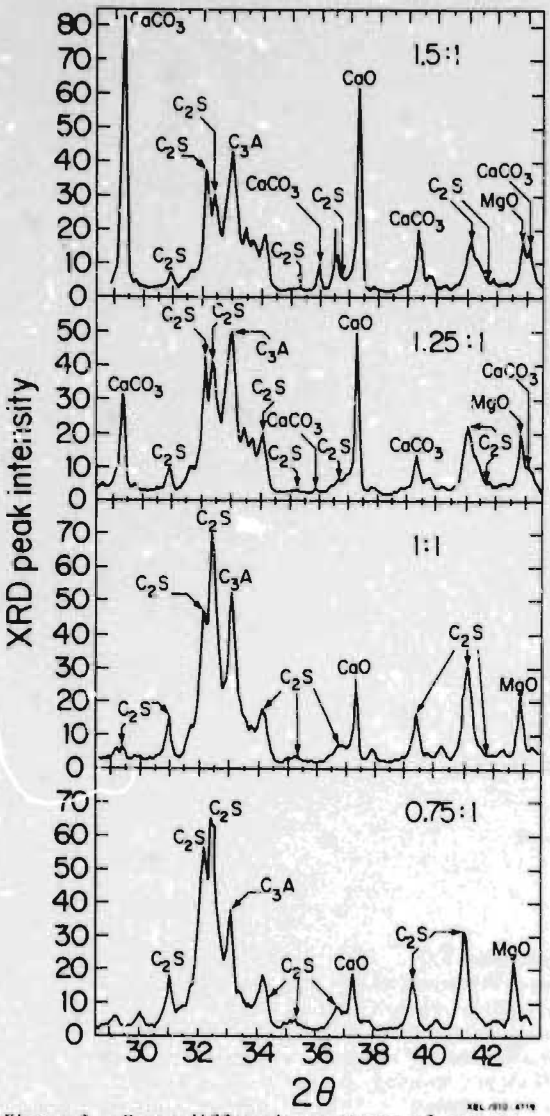

Figure 2. X-ray diffraction patterns of cements produced by heating limestone and Lurgi spent shale at 1000°C for 1 hr. Limestone-spent shale ratios range from 0.75:1 to 1.5:1.

Since the presence of gypsum in portland cement is known to accelerate early strengths, the 28-day strength of the 1:1 cement was also measured after addition of 5 percent gypsum. Using the coarse sand and a water-cement ratio of 0.52, this cement had a 28-day strength of 25.8 MPa, compared to 21.7 without gypsum.

PRACTICAL IMPLICATIONS FOR RETORT ABANDONMENT AND OTHER APPLICATIONS

The hydraulic cement described here could be used for plugging abandoned in-situ retorts, for on-site construction (buildings, treatment facilities, headframe, etc.) or sold outside of the oil shale region. This would minimize the amount of spent shale for disposal and lower the capital costs of an in-situ plant by providing a cheap construction material.

The Lurgi cement is projected to cost about $22 per Mg of cement or about a factor of three less than portland cement. The lower cost is due to the consumption of less energy and the use of smaller quantities of raw materials in the process. Less $CaCO_3$ goes into a ton of Lurgi spent shale cement than into a ton of portland cement, so less thermochemical energy is needed to decompose $CaCO_3$ and produce CaO. The lower temperature of calcining (1000°C rather than 1400-1500°C) also saves energy. Less energy is used grinding raw materials since less limestone is needed and the spent shale is already a powder. The clinker produced is softer than portland cement clinker, and requires less energy for final grinding. And finally, the Lurgi spent shale is a waste material which may be difficult or expensive to dispose of.

Even though the cost of Lurgi spent shale is lower than portland cement, it is still too high to fill 100% of the voids in an abandoned in-situ retort. About 220 to 350 kg of grout are needed per barrel of oil recovered to fill all of the voids. At $22 per Mg, this would cost $4.84 to $7.70 per barrel of oil for the material alone. However, such a grout could be used to form a plug in the retort, filling some fraction of the voids, or it could be used as an admixture in a slurry of spent shale or other lower cost grout. For example, replacing 10% of the grout material (untreated Lurgi spent shale) by Lurgi spent shale cement would increase the cost of the grouting operation by $0.48 to $0.77 per barrel. This level of addition appears reasonable and may be necessary to meet the permeability, permanence, and structural requirements for grouted retorts.

ACKNOWLEDGMENTS

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