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OIL SHALE

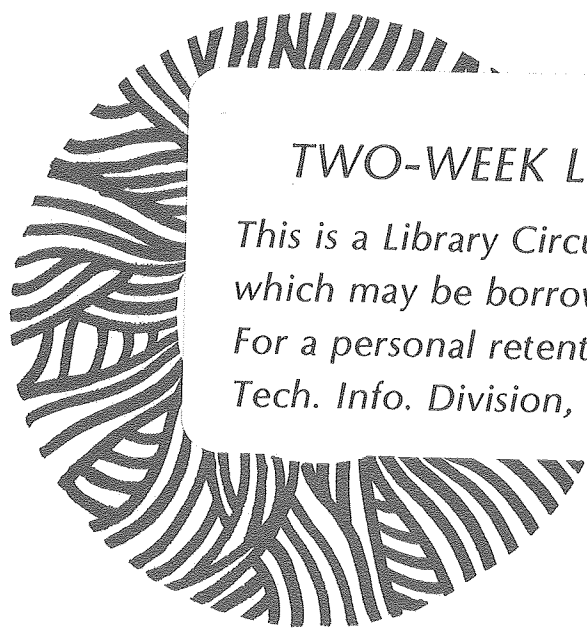
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INVESTIGATIONS ON HYDRAULIC CEMENTS
FROM SPENT OIL SHALE

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ABSTRACT

A process for making hydraulic cements from spent oil shale is described in this paper. Inexpensive cement is needed to grout abandoned in-situ retorts of spent shale for subsidence control, mitigation of leaching, and strengthening the retorted mass in order to recover oil from adjacent pillars of raw shale. A hydraulic cement was produced by heating a 1:1 mixture of Lurgi spent shale and CaCO_3 at 1000°C for one hour. This cement would be less expensive than ordinary portland cement and is expected to fulfill the above requirements.

Ein Verfahren zur Herstellung von hydraulischen Zementen aus ausgelaugten Öl-Schiefer ist dargestellt. Billiger Zement ist gewünscht um ausgebeutete in-situ Retorten zu verpressen. Der Zement soll sowohl das Einstürzen der Retorten als auch die Auflösung löslicher Stoffe zu verhindern und gleichzeitig die ausgelaugte Retorte zu verfestigen um die Ölgewinnung aus rohem Öl-Schiefer der benachbarten Abschnitte zu ermöglichen. Durch einstuündiges Erhitzen einer 1:1 Mischung von Lurgi ausgelaugtem Öl-Schiefer und CaCO_3 bei 1000°C kann ein hydraulischer Zement hergestellt werden, der billiger ist als herkömmliche Portland Zemente und von dem erwartet wird, dass er die obengenannten Anforderungen erfüllt.

Introduction

Current plans for oil shale development in the western United States call for a combination of surface and modified in-situ retorting. Surface retorting produces about 8 kg of spent shale per liter of oil recovered, depending on shale grade, for which environmentally safe and economic disposal must be found. Modified in-situ retorting consists of mining and surface retorting 20 to 40% of the oil shale, and explosively rubbleizing and retorting the rest of the material underground. This results in the formation of underground caverns or retorts filled with a weak and permeable rubble of spent shale. When such retorts are abandoned, groundwater quality can be degraded by leaching of in-situ spent shale, and retort overburden may subside. These problems may be solved by grouting the abandoned retorts to reduce permeability and increase strength. Adequate strengthening of abandoned retorts could also increase resource recovery by permitting recovery of oil from adjacent pillars of raw shale. These pillars, needed for structural integrity of retorts, contain about 45% of the oil shale, which is not recoverable unless retorts are grouted to adequate strength.

The void space to be grouted in in-situ retorts amounts to about 1.4 to 2.3 liters per liter of oil recovered, depending mainly upon the fraction of oil shale mined. Conventional grouts containing portland cement are considered too expensive for this application. Therefore, on one hand there is the problem of finding large quantities of inexpensive materials for grouting abandoned in-situ retorts, and on the other, of disposing of surface spent shale. The investigation described in this paper is aimed at the utilization of surface retorted spent oil shale for making less expensive hydraulic cements which would produce grouts with adequate strength and permeability characteristics for grouting in-situ retorts.

Colorado oil shales contain an abundance of dolomite, quartz, and feldspar, and therefore are not well-suited as raw materials for manufacture of portland-like cements. As shown below, some changes in the composition of the raw mix are necessary if cements having adequate hydraulic strength characteristics are to be made from spent Colorado oil shale. Sellers (1) obtained a patent on the production of portland cement from 1.8:1 mixtures of limestone and raw oil shale (corresponding to a 3:1 mixture of limestone and spent shale) by 1400-1500°C heat treatment. The high costs of materials and energy involved would not favor this process for the preparation of a hydraulic cement for grouting in-situ retorts.

Materials and Procedure

The spent shale used in this investigation was obtained from an experimental run on a raw Colorado oil shale which was retorted in the Lurgi retort in Germany. In this process, which is under consideration for surface retorting of Colorado oil shales, the retorted spent shale containing coke is burned to provide heat for the process. The retorting and the burning temperatures of the Lurgi spent shale used in this investigation were 530° and 700°C, respectively. Following the burning operation, the spent shale was collected in an electrostatic precipitator. The fineness, chemical, and mineralogical properties of the Lurgi spent shale are shown in Table 1 below.

TABLE 1. Properties of Lurgi Spent Shale.

Mineral present ^a	Chemical analysis, % ^b	Particle size, % ^c
Dolomite	Al ₂ O ₃ 7.2	>30.3 μm 0.6
Quartz	Na ₂ O 2.3	17.9-30.3 μm 2.1
Calcite	MgO 7.5	10.0-17.9 μm 4.9
Feldspar	SiO ₂ 32.0	6.6-10.0 μm 9.0
	CaO 21.8	3.94-6.6 μm 25.7
	Fe ₂ O ₃ 2.7	<3.94 μm 57.7
	Ignition loss 20.0	

^aanalysis by X-ray diffraction

^banalysis by low energy X-ray fluorescence for elements -- expressed as oxides. Method described in (2)

^cparticle size analysis supplied by Amoco (3)

X-ray diffraction analysis of the as-received sample of spent shale showed that besides quartz and feldspar, dolomite and calcite were still the principal minerals present. Loss on ignition of the material, due mainly to carbonate CO₂, was 20%. The presence of large quantities of calcite and dolomite in the spent shale, and absence of free MgO, CaO, and silicates of lime and magnesia, show that the retorting conditions, especially the retorting and burning temperatures, were not adequate to decompose dolomite and calcite, and form CaO. After ignition of the spent shale in a laboratory muffle furnace at various temperatures from 800 to 1000°C, large quantities of akermanite, Ca₂MgSi₂O₇, were formed. Thus, simple heat treatment of the spent shale caused dolomite, calcite, and the siliceous minerals to be converted to akermanite (which is not cementitious) with no free lime present. Since the presence of reactive calcium silicates or a mixture of free lime and reactive silica is essential for the formation of the cementitious calcium silicate hydrate (C-S-H), it is obvious why the heat-treated Lurgi spent shale did not develop any measurable strength on hydration.

A comparison of the chemical analysis of the Lurgi spent shale and a typical portland cement raw mix showed that the CaO:SiO₂ ratio of the former is less than 0.7 whereas for the latter, it is greater than 3.0. Temperatures of 1400-1500°C are required for the formation of C₃S, which is the principal compound in industrial portland cement. As discussed earlier, the high costs of materials and energy involved would not favor the manufacture of a portland cement-like composition from the Lurgi spent shale.

The second most abundant compound in ordinary portland cement is βC₂S. It is less reactive on hydration but requires a lower CaO:SiO₂ ratio and considerably lower temperature for its formation than C₃S. Another portland cement compound, C₃A, is highly reactive, and like βC₂S it is also formed at much lower temperatures than C₃S. It is conceivable, therefore, that cements of adequate strength may be produced if the composition of the raw mix containing the Lurgi spent shale is altered to a higher CaO/SiO₂ ratio in order to form βC₂S and C₃A as the principal compounds. Such cements, however, would not be portland cements because of the absence of C₃S.

The first experiments of this investigation consisted of preparing blends of Lurgi spent shale with a commercial-grade CaCO_3 powder in 1:1 proportions by weight, heating the mixture in an electrical muffle furnace at 900, 950, 1000, or 1100°C for one hour, grinding the resulting material and determining the mineral composition and strength characteristics of the cements thus produced. The second experiment was undertaken to determine the optimum CaCO_3 :spent shale ratio which would produce a cement having adequate strength characteristics when the raw mixture is heated at 1000°C for one hour. The mixtures investigated correspond to the CaCO_3 :Lurgi spent shale ratios 0.5, 0.75, 1.0, 1.25, 1.5 and 2.0.

Investigations were also carried out to find methods of increasing the strengths of mortars containing cements made from CaCO_3 -spent shale mixtures. In one experiment, the water-cement ratio of the test mortars was reduced from 0.625 to 0.52 by replacing the ASTM C109 standard sand by a coarser sand. In another experiment strength acceleration was achieved by addition of 5% gypsum to the cement which resulted in the formation of ettringite on hydration. It should be noted that formation of ettringite from C_3A contributes to the setting and hardening of portland cements. Also, since the same objective can be achieved by substitution of $\text{C}_4\text{A}_3\bar{\text{S}}$ for C_3A in the anhydrous cement composition, in one experiment 10% gypsum by weight of raw mix was added to a 1:1 CaCO_3 -spent shale mixture before the heat treatment. In this case, a higher temperature, namely 1250°C, was employed in order to obtain a well-sintered clinker containing $\text{C}_4\text{A}_3\bar{\text{S}}$.

Qualitative mineralogical analyses of the cements were carried out by X-ray diffraction, using $\text{Cu K}\alpha$ radiation at 40 KV, 30 mA. Free CaO was quantitatively determined by ASTM Method C114. Unless otherwise stated all the cements were ground to 90% particles $\leq 75\mu\text{m}$. Compressive strengths of the cements were determined by 2-inch mortar cubes which contained ASTM C109 standard sand (sand-cement ratio 2.75), and 0.625 water/cement ratio. Casting, curing, and testing of the mortars were done in accordance with ASTM Method C109.

Results and Discussion

The results of heat treatment of 1:1 mixtures of CaCO_3 and spent shale at 900, 950, 1000, and 1100°C are shown in Table 2.

The data show that in 1:1 mixtures of CaCO_3 and Lurgi spent shale, the formation of akermanite (the non-cementitious compound) was prevented, and that temperatures of the order of 1000° and 1100°C were adequate to form $\beta\text{C}_2\text{S}$ and C_3A , the compounds capable of forming the cementitious hydrates. Adequate 28-day strengths were obtained in the cements made at 1000° and 1100°C, the optimum temperature from standpoint of strength being 1000°C.

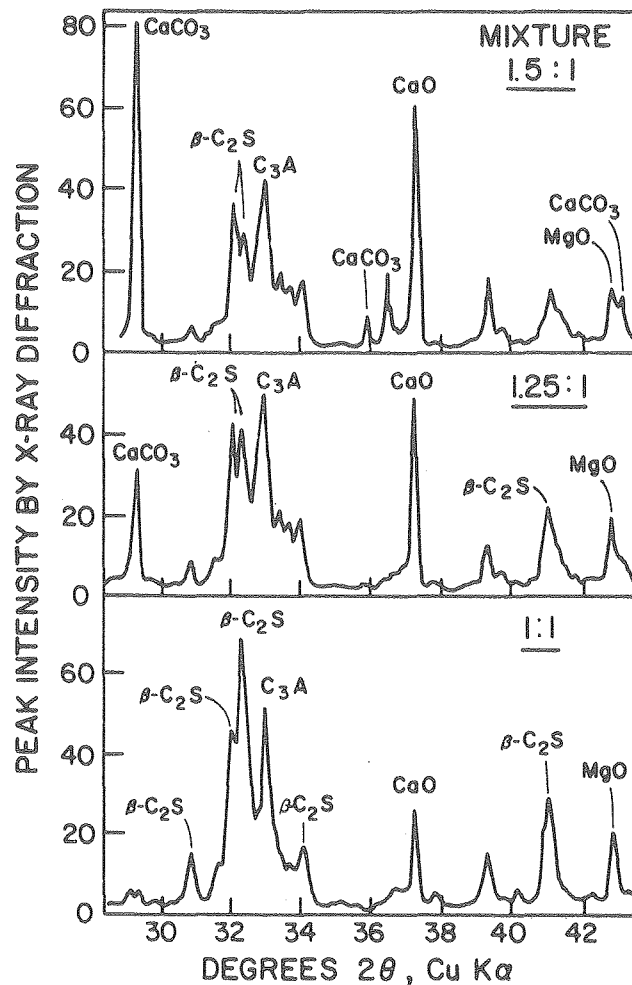
The results of experiments undertaken to determine the optimum CaCO_3 to spent shale ratio which would yield cements of good cementitious characteristics at 1000°C are shown in Fig. 1 and Table 3.

TABLE 2. Properties of Cements Made From 1:1 Mixtures of CaCO₃ and Lurgi Spent Shale.

	Temperature of heat treatment			
	900°C	950°C	1000°C	1100°C
<u>Minerals present</u>				
Akermanite	N	N	N	N
C ₃ S	N	N	N	N
β-C ₂ S	W	W	M	M
C ₃ A	W	W	W	W
CaCO ₃	VS	S	W	N
<u>Compressive strength, psi (MPa)</u>				
3 day	190(1.3)	280(1.9)	470(3.2)	295(2.0)
7 day	450(3.0)	630(4.3)	950(6.6)	650(4.5)
28 day	925(6.5)	1400(9.7)	2720(18.8)	2100(14.5)
N = none W = weak M = medium S = strong VS = very strong				

TABLE 3. Free Lime Content and Compressive Strength of Cements made from Various Proportions of CaCO₃ and Lurgi Spent Shale, 1 hr @ 1000°C.

Compressive Strength, psi (MPa)	CaCO ₃ :Spent Shale Ratio						
	2:1	1.75:1	1.5:1	1.25:1	1:1	0.75:1	0.5:1
3 day	120(0.8)	250(1.7)	140(0.9)	170(1.2)	340(2.3)	375(2.5)	poor
7 day	380(2.6)	430(3.0)	390(2.7)	395(2.7)	670(4.6)	455(3.1)	poor
28 day	840(5.8)	1210(8.3)	1200(8.3)	890(6.1)	2600(17.9)	1100(7.6)	poor
90 day	1310(9.0)	1690(11.7)	1910(13.2)	1600(11.0)	3340(23.0)	1720(11.9)	poor
Free CaO, %:	12.2	9.0	7.9	6.0	3.1	1.5	0.6



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Fig. 1. Mineralogical Analysis of Cements Made by Heating CaCO_3 -Lurgi Spent Shale Mixtures at 1000°C .

From the X-ray diffraction data in Fig. 1, it is obvious that 1:1 mixtures of CaCO_3 and spent shale, when heated at 1000°C for one hour, produced a material which contained little CaCO_3 , large quantities of $\beta\text{C}_2\text{S}$ and C_3A , and only a small quantity of unreacted free lime. Accordingly, this material gave the highest 28- and 90-day compressive strengths, namely 2600 psi (17.9 MPa) and 3340 psi (23.0 MPa) respectively. The progressive increase in strength under continuous moist curing conditions shows that the cement is hydraulic. Lower strength of the cements made from $\geq 1.25:1$ mixtures are attributed to large amounts of CaCO_3 and free CaO present.

The effect of lowering the water-cement ratio from 0.625 to 0.52 on the compressive strength of cements is shown in Table 4. Also shown in this table are data on the effect of gypsum additions, either directly to the cement, or indirectly through the raw mix before it is heat treated at 1000°C . In the latter case it was confirmed by X-ray diffraction analysis of the cement that the aluminat phase present was $\text{C}_4\text{A}_3\text{S}$ rather than C_3A .

TABLE 4. Effect of Water-Cement Ratio and Gypsum Additions on the Strength of Cements made from Mixtures of 1:1 CaCO₃ and Lurgi Spent Shale.

Water-Cement Ratio	0.625	0.52	0.52	0.52
Gypsum addition to cement	-	-	5%	-
Gypsum addition to raw mix	-	-	-	10%
<u>Compressive strength, psi (MPa):</u>				
7 day	670(4.6)	970(6.7)	1510(10.1)	2200(15.1)
28 day	2600(17.9)	3150(21.7)	3750(25.8)	4375(30.1)

The data in Table 4 show that a 17% reduction of water-cement ratio (from 0.625 to 0.52) brought about a proportional increase in the 28-day compressive strength (from 2600 to 3150 psi). Although the use of a coarser sand was responsible for the reduction of water-cement ratio in this experiment, similar results can be achieved through small additions of water-reducing admixtures. Since 0.485 is the standard water-cement ratio in the ASTM C109 for determination of the compressor strength of portland cement mortars, it is obvious that the cements made from 1000°C heat treatment of the 1:1 CaCO₃-spent shale mixture will have the potential of attaining a minimum of 3000 psi (20.7 MPa) compressive strength at 28 days. This happens to be the minimum 28-day strength requirement for the sulfate resisting portland cements as per ASTM C150. The sulfate-resisting portland cements, which have somewhat lower strength requirements than general-purpose portland cements, are recommended for use in mortars and concretes exposed to sulfated waters.

The data in Table 4 also show that strength gains of the order of 50% at 7 days and 20% at 28 days could be realized at 0.52 water-cement ratio when 5% gypsum addition probably made the formation of ettringite possible in the hydrated cement. Considerable strength gains were further obtained when the C₃A in the cement was replaced by C₄A₃S through 10% gypsum addition to the raw mix. Thus, the 7- and 28-day compressive strengths of the cement containing C₄A₃S and βC₂S were 2200 (15.1 MPa) and 4375 psi (30.1 MPa), respectively. It may be noted that the ASTM C150 Standard Specification requires minimum 2000 psi (13.8 MPa) and 3000 psi (20.7 MPa) compressive strengths from sulfate-resisting portland cement at 7 and 28 days, respectively. However, it should also be noted that the C₄A₃S-βC₂S cement was made at a higher temperature. Due to high energy and materials costs, such a cement may not be economical for grouting in-situ retorted shales. But the point is that by making suitable modification in the process, cements having structural characteristics approaching portland cement can be made from spent oil shales.

Energy Requirement and Cost

It is demonstrated above that a hydraulic cement of adequate strength can be made by heating 1:1 mixtures of CaCO₃ and Lurgi spent shale at 1000°C for one hour. As compared with portland cement, the limestone and energy requirement of the process are considerably less. Compared to 65% CaO in portland cement, this cement will contain less than 50% CaO. Since the heat energy required to decompose CaCO₃ to lime corresponds to 714 kcal per kg CaO, this cement represents a saving of 120 kcal per kg. Also, compared to 1400°C burning temperature for portland cement, the above described hydraulic cements will be made at 1000°C. At 50 kcal per 100°C heat energy savings, this represents a saving of 200 kcal

per kg. Thus a potential saving of 320 kcal per kg cement is indicated if rather than making portland cement, the Lurgi spent shale is used to make the hydraulic cements described in this report. Since the modern suspension preheater kilns for manufacture of portland cement require about 800 kcal per kg heat for the clinking operation, about 40% saving in heat energy is possible if the hydraulic cement of the type suggested here is made. Furthermore, the limestone requirement of this cement will be one-third of the limestone required for making portland cement from the Lurgi spent shale. Also, due to the fine particle size of the spent shale no energy will be needed for its crushing and grinding. Therefore, instead of attempting to make portland cement-like compositions for grouting abandoned in-situ retorts, it is recommended that hydraulic cement compositions described in this paper should be considered because of their considerably lower cost and adequate strength characteristics.

Acknowledgments

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