NEW HIGH TEMPERATURE CEMENTING MATERIALS FOR GEOTHERMAL WELLS: STABILITY AND PROPERTIES

**FINAL REPORT
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**For the
GEOTHERMAL MATERIALS GROUP**

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ABSTRACT

Potential high-temperature cements have been formulated and evaluated in terms of their properties for geothermal well cementing. Phase formation and compatibility in two major compositional regions were investigated in the temperature region between 200 and 400°C and pressures up to 69 MPa (10,000 psi). These were followed by an evaluation of properties of the cements formed. One area in the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ centered around the xonotlite-chrysotile join while the other area of interest centered around the anorthite composition in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. After numerous exploratory studies, the magnesia-containing mixtures were prepared by mixing a Class J cement with various sources of magnesia such as calcined chrysotile, or magnesium oxide. Calcium oxide and silica fine quartz powder were also added to adjust the compositions. The aluminous system cements were formulated from high-alumina cements which were mixed with various silica sources (Roy, et al., 1978).

The potential geothermal cements which have been developed have fulfilled the following general requirements:

- 24-hour compressive strength > 6.9 MPa (1000 psi),
- water permeability < 0.1 millidarcy,
- cement/steel bond strength > 0.07 MPa (10 psi),
- 96-day stability in hydrothermal water or 20% brine,
- noncorrosive to steel casing,
- 2-hour room temperature workability well within specifications,
- maintenance of pumpability at temperatures up to 350°F (177°C) for 4 hours.

These cements hold promise as new geothermal cements, but additional long-term testing is still needed to fully evaluate their true potential. Some samples have been tested for pumpability, which has been shown to be adequate. Some have been submitted to the National Bureau of Standards (NBS) for their standard testing program.

PERSONNEL

In addition to Dr. Della M. Roy, the principal investigator, the research was carried out by the following: Drs. Michael W. Grutzeck and Elizabeth L. White; graduate student, Christine A. Langton; and research technicians, K. G. Zimmerman and N. Hermanowicz. In addition, a small portion of the work was carried out by D. Wolfe-Confer and Dr. R. M. Smart.

I. INTRODUCTION

New high-temperature hydrothermally cured cement formulations for geothermal well applications are being sought in order to better utilize geothermal energy resources. Performance criteria for geothermal cements often exceed those currently specified for oil well cement technology. Therefore, the potential exists for significant improvement, with the objective of tailor-making cements that can withstand the high-temperature, high-pressure, and often-corrosive geothermal environment.

This study concentrated on two major compositional systems with the hope of finding suitable cements which formed stable phases outside the usual cement compositions but having adequate cementitious properties and high durability. After a considerable number of preliminary experiments (BNL, 1977, 1978a, 1978b, 1978c, 1978d, 1979), it was possible to narrow the study to two compositional areas. One area, in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, centers about anorthite, while the other, in the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$, centers about diopside (see Figs. 1, 2). Since a number of the compositions in these systems as well as the temperature range (up to 400°C) were different from previously investigated materials, much time and effort was devoted to the determination of phase stability. In addition to the physical and mechanical property studies, phase stability studies were especially important, since prolonged service under hydrothermal temperatures and pressures is likely to introduce unknown phase changes. The knowledge of these potential changes and their effects upon performance were therefore extremely important.

From the outset, certain criteria were specified and served as guidelines, setting minimum acceptable values. These criteria are taken from the original contract and listed here. Geothermally stable cementing products must have:

- high compressive strength $> 6.9 \text{ MPa}$ (1000 psi), 24 hours after placement;
- low permeability to water, < 0.1 millidarcy;
- cement/steel bond strength $> 0.07 \text{ MPa}$ (10 psi);
- maintenance of strength and low permeability at 400°C ;
- maintenance of pumpability at elevated temperature (350°F , 177°C).

Figure 1. Projection of Selected Compounds and Mixtures in the System $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ onto the Anhydrous Ternary Diagram $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. Areas of Interest for Hydrothermally Cured (200-400°C, 6.9 to 68.9 MPa in the Presence of Excess Water) Cements are Outlined

Figure 2. Projection of Selected Starting Compositions and Stable Compounds in the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ System onto the Anhydrous Ternary Diagram CaO-MgO-SiO_2 . Area of Interest for Hydrothermally Cured (200-400°C, 6.9 to 68.9 MPa in the Presence of Excess Water) Cements is Outlined

In the final formulations, these criteria have been exceeded by a significant margin. For the most part, these criteria were modest (except for the high temperature performance) and therefore it was possible to delineate substantial compositional regions, having acceptable properties.

The procedure was to first assess in a preliminary manner approximate cementing properties of some potential mixes, then carry out phase studies, and finally to complete property studies.

II. PHASE STUDIES

A. Starting Materials

Commercially available source materials were used whenever possible, along with parallel mixes from reagent grade oxides, in order to facilitate potential commercial applications as quickly as possible. CaO-MgO-SiO_2 mixtures were formulated from a Class J cement and calcined chrysotile. Compositional adjustments were made by adding oxide material (5-micrometer quartz and reagent-grade CaO). $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ mixtures were formulated from high-alumina cements and 5-micrometer quartz. Before reaching a decision on the above formulations, a variety of materials were investigated. Some of the highly reactive silica-rich compositional modifiers used included perlite (a manufactured expanded volcanic glass) and tripoli powder (a material having marine origins). A small amount of perlite could be added to make a lightweight product, but for the most part, mixtures were made without perlite. It was found that run products in the magnesia-containing system were more independent of starting materials compared to those in the alumina-containing system. Reaction products in the alumina system were very dependent on starting materials. In addition, mixtures in both systems were also made from reagent grade oxides and run under identical conditions as the commercial based mixtures. These oxide mixtures served as a check on phase stability, giving a better feeling for phase stability/equilibria. The mixing and/or curing fluid used in all experiments was either a saturated solution of reagent grade NaCl mixed with deionized water, hereafter referred to as brine, or deionized water, hereafter referred to as water.

Starting materials also included B_2O_3 stabilized β - C_2S^* , other silica modifiers (silicic acid, dehydrated Ludox** gels), and an alimina modifier, metakaolinite. The latter was prepared by heating Kaopaque 30 (high purity kaolinite) at $750^\circ C$ for 4 hours. The final product was amorphous with a bulk composition equivalent to dehydrated kaolinite. Chrysotile serpentine was calcined at $800^\circ C$ for 6 to 10 hours to produce a reactive mixture of very fine grained amorphous material, forsterite, and some residual quartz. Figures 1 and 2 show the range of compositions studied in the final phases of the contract. See earlier quarterly reports and Appendices B and C for earlier preliminary work. Not all these materials were as successful as others, and most of them were eliminated. The final formulations, mentioned in the Introduction, were chosen for ease of formulation, availability of starting materials, and superior physical properties.

Blaine specific surface and density measurements were made on the cements and some of the additives used in this study. These are listed in Table 1.

B. Sample Preparation Methods

Two sample preparation techniques were generally employed, one primarily for phase relation determinations, the other for physical property measurements. For phase determinations small samples were placed in noble metal tubes (5x25 mm) in a closed system (tubes were welded then weighed before and after curing) or in an open system (tubes were mechanically crimped at each end). Within each system samples were prepared either as dry samples, dry samples plus liquid, or as a paste. The liquid, a required amount of either water or brine, was inserted with a hypodermic needle. For those tubes which were merely crimped, water from the reaction vessel had free access to the samples. For those tubes which were welded with a torch, the system was "closed" and isolated from additional water sources. Occasionally the powder samples, without any water, were placed into crimped noble metal tubes and allowed to react with the liquid which seeped into the sample during hydrothermal

*Cement nomenclature, C = CaO, S = SiO_2 , A = Al_2O_3 , M = MgO, H = H_2O .

**Ludox ammonium stabilized colloidal silica-AS-40, DuPont, dehydrated at $200^\circ C$.

Table 1

Blaine Specific Surface and Density Measurements

Material*	Date manufactured	Blaine cm ² /g	Density g/cc
Class J oil well cement, J-1	1977-78	3470	2.93
Class J oil well cement, J-2	1979	1980	2.70
Aluminous cement, S-1	?	--	2.59
Aluminous cement, S-2	1979	2740	2.70
Aluminous cement, R-1	1977	4900	3.12
5- μ m quartz		15000	2.65

*Manufacturer's cement specifications are listed in Appendix G.

treatment. These results were comparable with other preparation techniques, except when brine was the reacting fluid, in which case NaCl was removed from the noble metal capsule. A more conventional approach was used in the second preparation technique. Slurries were mixed with either water or brine, placed in 25 x 50-mm plastic molds, allowed to cure at room temperature and elevated humidity for a given period of time (30 minutes to 24 hours), removed from the molds, and placed in large but conventional externally heated hydrothermal vessels. For bond strength to rock and steel similar procedures were used, modified only slightly to better duplicate the geothermal environment. In both measurements sample containers of some type of host material were used. For bond strength to rock, hollow rock cylinders (51 mm O.D., 19 mm I.D.) were filled with cement slurry, fitted with stainless steel end caps (to minimize leakage), and immediately placed in externally heated 500-cc hydrothermal pressure vessels. The pressure medium was deionized water; reactions were typically run at 300° to 400°C and up to 10,000 psi (68.9 MPa). For bond strength to steel, 19 mm steel rods [both as-received (metallic) and rusted] were placed in the center of 51 mm I.D. steel shells which were filled with cement

slurry, held in place, and fitted with end caps, to minimize leakage, and immediately placed in similar externally heated 500-ml hydrothermal pressure vessels.

Samples placed in noble metal tubes were mixed by hand; the larger samples were mixed using either the ASTM-C305 standard or the API standard mixing procedures. Mixing speeds were ~140 rpm and between 3000 and 9000 rpm, respectively. The larger samples were puddled as they were loaded and subsequently vibrated for 1 minute at 60 cps. Furnaces were generally preheated so as to ensure a more rapid attainment of temperature and pressure. Pressure and temperature equilibrium was attained within 12 to 24 hours.

C. Characterization of Phases

1. CaO-SiO₂-H₂O System. For the powdered samples which were run in crimped gold tubes and cured at $(385 \pm 5)^\circ\text{C}$, xonotlite $[\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2]$ dehydrated to wollastonite $(\beta\text{-CaSiO}_3) + \text{H}_2\text{O}$ at 2500 psi (17 MPa), but xonotlite was still stable at 25,000 psi (170 MPa). These data placed the dehydration temperature at a somewhat lower temperature than those previously reported by Buckner, et al. (1960), Roy and Johnson (1965), and Roy, et al. (1979). Mixtures containing major amounts of xonotlite and/or foshagite had enhanced cementitious properties. Wollastonite, which formed as large bladed crystals, generally tended to reduce strength, as will be discussed later. Reaction products were comparable for all starting materials using $\beta\text{-Ca}_2\text{SiO}_4$ ($\beta\text{-C}_2\text{S}$) + various silica sources. Mixtures of $\beta\text{-C}_2\text{S}$ + diatomite tended to be the most reactive.

For those mixtures hydrothermally cured at 250°, 300°, 350°C, and 68.9 MPa (10,000 psi), again a good cementitious composition contained foshagite as fibers and xonotlite as fine needles. The fine interlocking needles of xonotlite prepared from $\beta\text{-C}_2\text{S}$ + diatomite with a bulk composition of 48 weight percent CaO and 52 weight percent SiO₂ were indicative of some of the best cementing characteristics (Figure 3c). Truscottite $[\text{Ca}_2\text{Si}_4\text{O}_9(\text{OH})_2]$ was present in the 250°, 300°, and 350°C cured products in varying amounts depending on the silica content and degree of silica crystallinity of the starting materials. Its presence in the mixtures was not detrimental. For a tabulation of the data, see Table 2, and microstructures in Figure 3.

Fig. 3A—Mats of Wollastonite Blades Formed From 48% CaO, 52% SiO₂ Cured at 400°C and 68.9 MPa for 10 Days.

Fig. 3B—Large Fibers of Foshagite Fibers Embedded in Fine Needles of Xonotlite Formed from 58% CaO, 42% SiO₂ Cured at 400°C, 68.9 MPa for 10 Days.

Fig. 3C—Interlocking Needles of Xonotlite Formed from β -C₂S + Tripoli at 48% CaO, 52% SiO₂ Cured at 350°C, 68.9 MPa for 10 Days.

Fig. 3D—Hexagonal Plates of X-Phase Formed from S Calcline Aluminate Cement and 5 μ Min-U-Sil, 13% CaO, 35% Al₂O₃, 50% SiO₂ Cured at 400°C, 68.9 MPa for 10 Days.

Fig. 3E—Mostly Triclinal Anorthite and Some X-Phase Formed from β -C₂S, Metakaolinite, Silica Cured at 400°C, 68.9 MPa for 10 Days.

Fig. 3F—Nearly Pure Diopside Formed from β -C₂S and Calcined Chrysotile Paste Cured at 400°C, 68.9 MPa for 10 Days.

Figure 3. Microstructures of CaO-SiO₂-H₂O and CaO-Al₂O₃-SiO₂-H₂O Hydrothermal Products

Table 2

Runs used for Determinations of Phase Assemblages Crystallizing in a Portion of the Join $\text{CaO-SiO}_2\text{-H}_2\text{O}$

Mole Ratio	Composition (weight %)		Starting Materials ²	Temp. ($^{\circ}\text{C} \pm 5^{\circ}$)	Pressure (MPa ± 1)	Time (days)	Phases Present at end of Run ^{3,4} m = minor amounts**
	CaO	SiO ₂					
2:1	65.12	34.88	$\beta\text{-C}_2\text{S}$	220	68.9	14	unknown
4:3	55.45	44.55	$\beta\text{-C}_2\text{S} + \text{T}$	"	"	"	11 $\bar{\text{A}}\text{T}$ + unknown
3:2	58.34	41.66	"	"	"	"	11 $\bar{\text{A}}\text{T}$ + $\bar{\text{A}}\text{F}$ + SC
1:1	48.28	51.72	"	"	"	"	X + m11 $\bar{\text{A}}\text{T}$
5:6	43.75	56.25	"	"	"	"	X + 11 $\bar{\text{A}}\text{T}$
2:3	38.36	61.64	"	"	"	"	11 $\bar{\text{A}}\text{T}$ + TR + G(?)
3:5	35.90	64.10	"	"	"	"	TR + 11 $\bar{\text{A}}\text{T}$ + G(?)
2:1	65.12	34.88	Oxides	400	68.9	7	DE + X
			$\beta\text{-C}_2\text{S} + \text{T}$	400	"	7	X + mDE
			Oxides	350	"	7	DE + U
3:2	58.34	41.66	Oxides	400	68.9	3	X + F
			"	400	"	10	X + F
			$\beta\text{-C}_2\text{S} + \text{T}$	400	68.9	3	X + F + mWO + m $\beta\text{-C}_2\text{S}$
			"	400	"	10	F + X + mWO + mCA
			"	400	172.	10	X
			"	400	17.2	10	F + WO + X
			"	350	68.9	10	F + X + CA
			"	300	"	10	F + X + SC + U
			"	250	"	10	X + SC
4:3	55.45	44.55	Oxides	400	68.9	3	X + WO + F
			"	400	"	10	X + WO + F
			$\beta\text{-C}_2\text{S} + \text{T}$	400	"	3	F + X + WO + m $\beta\text{-C}_2\text{S}$
			"	400	"	10	X + F + WO
			"	400	172.	10	X
			"	400	17.2	10	W + X + F + mCA
			"	350	68.9	10	X + F + CA
			"	300	"	10	X + F + mSC
			"	250	"	10	X + SC
1:1	48.28	51.72	Oxides	400	68.9	3	X
			"	400	"	10	X + WO
			$\beta\text{-C}_2\text{S} + \text{T}$	400	68.9	3	X + WO + $\beta\text{-C}_2\text{S}$
			"	400	"	10	X + WO
			"	400	172.	10	X + WO
			"	400	17.2	10	WO
			"	350	68.9	10	X + mWO
			"	300	"	10	X
5:6	43.75	56.25	Oxides	400	68.9	3	X
			$\beta\text{-C}_2\text{S} + \text{T}$	400	68.9	3	X + WO + CR + $\beta\text{-C}_2\text{S}$
			"	400	"	10	X + WO
—	40.00	60.00	J	400	68.9	10	WO + X + CA
			"	350	"	10	X + TR + CA + SC
			"	300	"	10	X + TR + SC
2:3	38.36	61.64	Oxides	400	"	3	WO + mTR
			$\beta\text{-C}_2\text{S} + \text{T}$	400	68.9	3	W + TR
3:5	35.90	64.10	Oxides	400	"	3	X + TR + WO
			"	400	"	10	WO + CR
			$\beta\text{-C}_2\text{S} + \text{T}$	400	"	3	WO + TR + CR + $\beta\text{-C}_2\text{S}$
			"	400	"	10	WO + TR
			"	350	"	10	X + TR + CA + SC
			"	300	"	10	TR + SC
1:2	31.82	68.18	Oxides	400	68.9	3	CR + AM
			"	400	"	10	X + WO + CR
			$\beta\text{-C}_2\text{S} + \text{T}$	400	68.9	3	WO + CR

**Abbreviations, see Key, p. 10

2. CaO-Al₂O₃-SiO₂-H₂O System. Experiments in the system: CaO-Al₂O₃-SiO₂-H₂O (C-A-S-H) (Table 3) were carried out between 200 and 400°C at pressures ranging from 17.2 to 68.9 MPa (2500 to 10,000 psi) to map out phase relationships both above and below the critical point of water. Two areas within the system C-A-S-H which have demonstrated marked cementitious properties are Regions I and II which are outlined in Figure 1. Within Region I the addition of up to 10 percent Al₂O₃, as boehmite [AlO(OH)], and 25-45 percent Al₂O₃ in Region II affected the stability of the calcium silicate phases formed. Within Region I there were slight shifts in the 2θ values for both xonotlite and truscottite to lower values, and wollastonite appeared to be more stable than xonotlite down to temperatures of at least 385°C. The addition of 20 percent Al₂O₃ resulted in the crystallization of the hydrogarnets with compositions near grossular (Ca₃Al₂Si₃O₁₂) from 400°C curing. After 300°C curing hibschite [Ca₃Al₂(SiO₄)_{3-x}(OH)_{4x}] was produced. The area of most interest, Region II, is within the stability field of anorthite (CaAl₂Si₂O₈), in which was formed an anhydrous phase, hexagonal anorthite, found to have cementitious properties. This region excludes the hydrogarnet compositions, which do not have favorable cementing properties.

A calcium aluminate cement, brand R, had favorable strength properties when the pure cement was hydrothermally cured. However, another aluminate cement, brand S, had less favorable properties as a pure cement paste when cured hydrothermally. When the compositions of both cements were adjusted to approximately 50 wt. percent SiO₂, near the anorthite composition, then the brand S cement paste was much stronger after hydrothermal curing. Further properties studies continued with brand S cement.

The alumina system is very sensitive to starting materials. When a Class J cement was mixed with metakaolin it produced triclinic anorthite which had little strength or cementitious properties. When either aluminate cement was mixed with 5-micrometer quartz to form a bulk composition near anorthite, hexagonal anorthite was produced. Once it became apparent that the hexagonal anorthite phase held promise as a potential geothermal cement, larger cement samples were prepared and tested for their physical properties.

3. CaO-MgO-SiO₂-H₂O System. Experiments in the system CaO-MgO-SiO₂-H₂O (C-M-S-H) were also carried out at temperatures between 200° and 400°C and at pressures ranging from 17.2 to 68.9 MPa (2500 to 10,000 psi). In contrast to the delineated Regions I and II for the C-A-S-H system, there appears to

KEY FOR TABLES 2, 3, AND 4

¹All hydrothermally cured samples crystallized in the presence of excess H₂O in noble metal tubes unless otherwise specified.

²Starting Materials:

Oxides: reagent-grade oxides with Al₂O₃ added as AlO(OH)
 R and S: calcium-aluminate commercial cements
 J: Class J oil well cement
 MK: metakaolinite (amorphous Al₂Si₄O₁₁)
 Min: 5 μm quartz
 P: perlite -- expanded volcanic glass (ca 73% SiO₂, 18% Al₂O₃, 9% CaO)
 T: diatomite (amorphous silica powder having a marine origin).
 B-C₂S: B₂O₃-stabilized dicalcium silicate Ca₂SiO₄
 CC: calcined chrysotile

³Product Phases:

AF = afwillite, Ca₃(SiO₃OH)₂·2H₂O
 AH = hexagonal anorthite, CaAl₂Si₂O₈
 AM = x-ray amorphous material
 AN = antigorite, Mg₃Si₂O₅(OH)₄
 AT = triclinic anorthite, CaAl₂Si₂O₈
 B-C₂S = B₂O₃-stabilized, Ca₂SiO₄
 BI = bicchulite, Ca₂Al₂SiO₇·H₂O
 BO = boehmite, AlO(OH)
 CA = calcite, CaCO₃
 CH = chrysotile, Mg₃Si₂O₅·(OH)₄
 CO = corundum, Al₂O₃
 CR = cristobalite, SiO₂
 DE = dellaite, Ca₆Si₃O₁₁(OH)₂
 DI = diopside, CaMgSi₂O₆
 F = foshagite, Ca₄Si₃O₉(OH)₂
 GR = grossular, Ca₃Al₂Si₃O₁₂
 G = gyrolite, Ca₄(Si₆O₁₅)(OH)₂·3H₂O
 HG = hydrogrossular: comp. varying between grossular and hibschite
 HI = hibschite, Ca₃Al₂Si₂O₈(OH)₄
 MO = monticellite, CaMgSiO₄
 Q = quartz, SiO₂
 SC = scawtite, Ca₇Si₆(CO₃)O₁₈·2H₂O
 T = tobermorite, Ca₅(Si₆O₁₈H₂)·4H₂O
 TA = talc, Mg₃Si₄O₁₀(OH)₂
 TM = tremolite, Ca₂Mg₅Si₈O₂₂(OH)₂
 TR = truscottite, Ca₆Si₁₀O₂₄(OH)₂
 U = unidentified peaks -- x-ray pattern
 WA = wairakite, Ca(Al₂Si₄)O₁₂·2H₂O
 WO = wollastonite, CaSiO₃
 X = xonotlite, Ca₆Si₆O₁₇(OH)₂
 m = minor amount detected

⁴Powder diffractometer x-ray analyses were used to determine the phases present.

Table 3

Runs Used for Determination of Phase Assemblages Crystallizing in a Portion of the System
 $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (1)

Mixture No.	Composition CaO Al ₂ O ₃ SiO ₂ (wt %)			Starting materials (2)	Temp (°C ± 5)	Pressure (MPa ± 1)	Time (days)	Phases present at end of run (3,4) m = minor amounts**
10	27	10	63	Oxides	400	68.9	10	TR + mWO + mCR
				"	350	"	"	TR
				"	300	"	"	TR
11	36	10	56	Oxides	400	68.9	10	WO + CR
				"	350	"	"	X + TR
				"	300	"	"	X + TR + mAH
12	45	10	45	Oxides	430	68.9	10	WO
				"	350	"	"	X
				"	300	"	"	X
13	40	20	40	Oxides	400	68.9	10	HG + AT
				"	400	172.	"	= HI
				"	400	17.2	"	= GR
14	32	20	48	Oxides	400	68.9	10	X + WO + AT
				"	400	172.	"	WO + X + AT
				"	400	17.2	"	WO + AT
15	21	30	49	Oxides	400	68.9	10	AT
				"	400	172.	"	AT
				"	400	17.2	"	AT
8	30	30	40	Oxides	400	68.9	10	AT + HG
2	25	45	30	Oxides	400	68.9	10	AT + BI + BO + CO
3	32	58	10	Oxides	400	68.9	10	BI + C ₆ A ₃ H ₃ + CO + BO
7	10	40	50	Oxides	400	68.9	10	AT + AH + CR
E	13	37	50	S + Min	500	68.9	10	AH + Q
				"	400	"	"	AH + Q
				"	400	"	30	AH + Q
				"	400	172.	10	AH + Q
				"	400	17.2	10	AH + Q
				"	350	68.9	10	AH + Q
				"	300	6.9	10	AH + Q
E	13	37	50	S + Min	220	68.9	15	AH + Q
E	13	37	50	β-C ₂ S + MK	400	6.9	10	AT
				"	400	68.9	30	AT
				"	400	17.2	10	AT + mAH
				"	350	68.9	10	AT + mAH
				"	300	68.9	10	AH + AT
E	13	37	50	S + Min	400	68.9	10	AH + AT
				β-C ₂ S + MK + BO	400	68.9	10	AT + BI + BO
A*†	12	23	65	R + Min	390	20.7	4#	Q + AH
B*†	9	26	65	S + 5%P + Min	380	20.7	10	Q + AH + BO
C*†	16	29	55	R + Min	390	20.7	4#	Q + AH
D*†	12	33	55	S + 5%P + Min	380	20.7	10#	AH + Q + BO
E*†	13	37	50	S + M	400	9.65	3	AH + Q + BO
				"	365	9.65	6.5	AH + Q + WA
F*†	19	36	45	R + Min	390	20.7	4	AH + Q
G*†	14	41	45	S + 5%P + Min	380	20.7	10#	AH + Q
E*†	34	61	5	R	380	20.7	5	BI + C ₃ AH ₆ + BO surface BI + C ₃ AH ₆ + BO + Al ₂ O ₃ inside

#Temperature maintained; pressure reduced to 1 MPa for half time of experiment.

*Water/solid ratio = 0.45.

**Abbreviations, key p. 11.

†Larger samples cured in 500°C autoclave.

Table 4

Runs Used for Determination of Phase Assemblages Crystallizing in a Portion of the System
CaO-MgO-SiO₂-H₂O

Mixture No.	Composition CaO MgO SiO ₂ (wt %)			Starting materials (2)	w/s	Temp (°C ± 5)	Pressure (MPa ± 1)	Time (days)	Phases present at end of run (3,4) m = minor amounts**
P*	32	10	58	J + CC	2.0	400	68.9	10	X + WO
				"	"	350	"	"	X
				"	"	300	"	"	X
				"	"	250	"	14	X
				"	"	200	"	"	X + Q
Q*	24	20	56	J + CC	2.0	400	"	10	DI
				"	"	350	"	"	X + DI
				"	"	300	"	"	X + mCH
				"	"	250	"	14	X
				"	"	200	"	"	X
R*	16	30	54	J + CC	2.0	400	"	10	DI + MO
				"	"	350	"	"	DI + X + CH
				"	"	300	"	"	X + CH
				"	"	250	"	14	X + AN
				"	"	200	"	"	X + AN
S*	52	10	38	β-C ₂ S + CC	2.0	400	"	10	DE + MO
				"	"	350	"	"	MO + mDE
				"	"	300	"	"	X + DE
				"	"	250	"	14	DE + U
				"	"	200	"	"	DE + U
T*	39	20	41	β-C ₂ S + CC	2.0	400	"	10	MO + DI
				"	"	350	"	"	MO + DI
				"	"	300	"	"	X + CH
				"	"	250	"	14	DE + AN + X
U*	26	30	44	β-C ₂ S + CC	2.0	400	"	10	DI + MO
				"	"	350	"	"	MO + DI
				"	"	300	"	"	CH + X
				"	"	250	"	14	X + DE + AN
				"	"	200	"	"	U
MCS-1	30	22	48	J + Min + MgO	0.45	400	"	7	X + CH + CA
				"	"	300	"	"	X + mCH + mSC
MCS-2	24	18	58	J + Min + MgO	0.45	400	"	"	X + mTA + mDI + mβ-C ₂ S
				"	"	300	"	"	SC + TA + mQ + mβ-C ₂ S + mX
MCS-3	23	17	60	J + Min + MgO	0.45	400	"	"	X + TA + mDI + mQ + mCH
				"	"	300	"	"	SC + TA + Q + mβ-C ₂ S
MCS-4	22	16	62	J + Min + MgO	0.45	400	"	"	X + TA + DI + mQ + mCH
				"	"	300	"	"	SC + Q + TA + mβ-C ₂ S
MCS-5	26	19	55	J + Min + MgO	0.45	400	"	"	X + TA + mCA + mDI + mCH
				"	"	300	"	"	X + SC + mTA + mDI inside
				"	"	300	"	"	X + TA + mSC surface
MCS-11	30	22	48	Oxides	0.45	400	"	"	MO + DI + X + mQ + mTA + mCH
				"	"	300	"	"	X + CH + DI + mTA
MCS-12	24	18	58	Oxides	0.45	400	"	"	X + TA + DI + mTR + mTM
				"	"	300	"	"	DI + TA + X + mCH + mQ + mTR
MCS-13	23	17	60	Oxides	0.45	400	"	"	TA + X + DI + Q + mTR
				"	"	300	"	"	X + Q + DI + TA + TR
MCS-14	22	16	62	Oxides	0.45	400	"	"	TA + Q + X + TR
				"	"	300	"	"	Q + DI + X + TA + SC + TR
MCS-15	26	19	55	Oxides	0.45	400	"	"	DI + X + TA + mCH + mTM
				"	"	300	"	"	X + DI + CH + mTA

Table 4 (continued)

Mixture No.	Composition CaO MgO SiO ₂ (wt %)			Starting materials (2)	Temp (°C ± 5)	Pressure (MPa ± 1)	Time (days)	Phases present at end of run (3,4) m = minor amounts
MCS-6*	33	22	45	J + Min + MgO	400	68.9	10	AK + X + MO
MCS-22*	24	18	58	J + Min + MgO	400	"	"	X + TA + m β -C ₂ S + mDI + mCA
MCS-23*	23	17	60	J + Min + MgO	400	"	"	X + TA + mCH + mQ + mDI
MCS-24*	22	16	62	J + Min + MgO	400	"	"	X + TA + Q + DI + mTR
								unknown 2 θ = 28.5, 23.10
MCS-25*	26	19	55	J + Min + MgO	400	"	"	X + TA + DI + mCH
MCS-18*	34	15	51	J + MgO	400	"	36	X + CH + mCA
				"	400	"	63	DI + X + CA + mCH + mMO
				"	400	"	96	X + CH + CA
19*	28	29	52	J + Min + MgO	400	"	36	X + mCH + mCA
				"	400	"	63	DI + X + CH + mMO + mCA
				"	400	"	98	X + DI + CH + CA
20*	48	10	52	J + MgO + CaO	400	"	63	X + CH + CA
Saturated NaCl used in mixing water:								
MCS-1*	30	22	48	J + Min + MgO	400	68.9	7	DI + NaCl + MO + mX + mCA
				"	300	"	"	NaCl + SC + CH + mQ + mX
MCS-2*	24	18	58	"	400	"	"	X + NaCl + TA + mDI + mCA
				"	300	"	"	X + NaCl + SC + mTA
MCS-3*	23	17	60	"	400	"	"	X + TA + NaCl + mDI + mCA
				"	300	"	"	NaCl + SC + TA + mQ + C
								+ mDI + mDI
MCS-4*	22	16	62	"	400	"	"	NaCl + X + mTA + mDI + mCA
				"	300	"	"	NaCl + SC + Q + mTA
MCS-5*	26	19	55	"	400	"	"	DI + NaCl + mCA + mTA
				"	300	"	"	NaCl + X + SC + mCH
MCS-11*	30	22	48	Oxides	400	"	"	DI + NaCl + MO + Q
				"	300	"	"	NaCl + X + CH + mTA + mSC
MCS-12*	24	18	58	"	400	"	"	DI + TA + NaCl + TR + X
				"	300	"	"	NaCl + DI + X + CH + TA + mTR
								+ mSC
MCS-13*	23	17	60	"	400	"	"	NaCl + DI + TA + Q + mX
				"	300	"	"	NaCl + TR + Q + DI + TA + X
								+ SC
MCS-14*	22	16	62	"	400	"	"	NaCl + DI + Q + TA + mX
				"	300	"	"	NaCl + Q + TR + TA + DI + X
								+ mSC
MCS-15*	26	19	55	"	400	"	"	DI + NaCl + mX + mTA
				"	300	"	"	NaCl + X + DI + TM + TA
18*†	34	15	51	J + NgO	400	"	63	X + DI + CA + mCH
				"	300	"	"	SC + X + CH
19*†	28	20	52	J + Min + MgO	400	"	"	X + DI + CH + CA + mTA
				"	300	"	"	X + CH + mSC
20*†	38	10	52	J + Min + MgO	400	"	"	X + CA + CH + DI
				"	300	"	"	SC + X + CH + mDI

*Water/solid ratio = 0.45.

†Larger samples cured in 500-cc autoclave.

be a broad region along the xonotlite-chrysotile join which has shown promising geothermal cementing properties. The area of interest falls up to and including the diopside composition. Phases formed from some of the mixtures after curing at elevated temperatures and pressures within these areas are summarized in Table 4. Between 300° and 400°C, over the pressure range studied, an anhydrous silicate, diopside, readily crystallized under hydrothermal conditions. In the magnesium system, however, the reaction products tend to be independent of starting material and are more likely to be approaching equilibrium. Mixtures made from a Class J cement adjusted with CaO and MgO had similar phase products as mixtures made with all reagent-grade oxides (CaO, MgO, and micro-sized quartz). The products were also similar when calcined chrysotile was mixed with a Class J oil well cement.

A sample cured for 24 hours, with a composition near diopside, met the 24-hour strength and permeability requirements set up initially in this study even though diopside was not detected after short-time curing at 400°C.

In order to determine potential reaction products from commercial cements, where reactions proceed slowly, several other starting materials had been used. These alternate materials were also used in an attempt to alleviate problems of impurities, such as the occurrence of carbonate ions within the cement, and to determine their effect upon the equilibrium relationships. Compositions of (a) cement-based and (b) oxide mixtures are given in Table 5. Previous data with a mixture of calcined chrysotile as a starting material gave similar results.

The cement-based and oxide mixtures have equivalent compositions (neglecting CO₂ and trace components). Mixtures were adjusted to straddle joins which seemed to hold promise, not only as potentially geothermal cements, but also as having importance in interpreting phase relationships. Eight sets of experiments were carried out for each composition: two equivalent mixtures at each composition (Table 5), run at two temperatures (300° and 400°C), with two curing solutions (deionized water and a saturated brine solution). The run products (summarized in Table 4) are discussed below.

(a) Deionized Water: 300°C Curing. Reacted mixtures prepared from Class J cement were found to contain scawtite [Ca₇Si₆O₁₈(CO₃)·2H₂O] in varying amounts. In addition, there was an inverse relationship between the amount of scawtite and xonotlite. Scawtite increased as xonotlite decreased. This apparently resulted from the relatively small compositional difference

Table 5

Weight Percent of Starting Materials

Mixture w/s = 0.45	Class J cement	CaO	MgO	SiO ₂
MCS-1	75	--	22	3
MCS-5 (25)*	65	--	19	16
MCS-2 (22)*	60	--	18	22
MCS-3 (23)*	57.5	--	17	25.5
MCS-4 (24)*	55	--	16	29
MCS-6	75	3	22	--
MCS-11	--	30	22	48
MCS-15	--	26	19	55
MCS-12	--	24	18	58
MCS-13	--	23	17	60
MCS-14	--	22	16	62

*Identical to MCS-5 etc., except that mixture was formulated from carbonate-free Class J cement.

(except for CO₂ present in scawtite).* Scawtite was dominant in mixtures 2, 3, and 4; xonotlite was dominant in mixtures 1 and 5 with the appropriate companion phase playing a relatively minor role. Talc was found in all mixtures, increasing slightly as the mixture became more silica rich. Chrysotile was a major constituent in mixtures 1 and 5, which had the least silica. Unreacted quartz increased as the mixtures became more silica rich.

In contrast, the corresponding oxide mixtures did not contain scawtite. This was due to the absence of a carbonate impurity in the oxide components. Xonotlite was again a major phase in compositions 11 and 15 (equivalent to cement mixtures 1 and 5, etc.) showing a gradual decrease as the mixture became more silica rich. Diopside became a dominant phase in mixtures 12 to 14 as xonotlite becomes minor. Chrysotile decreased and talc increased as the mixtures became silica rich. Unreacted quartz dominated the products of the most silica rich mixture, MCS-14, showing a gradual increase from mixtures 11 to 14.

*Harker (1965) has defined the stability limits of scawtite within this pressure-temperature region, and it is logically formed in the presence of carbonated lime present in the Class J cement.

(b) Deionized Water: 400°C Curing. At this higher temperature, xonotlite and chrysotile were dominant in the MCS-1 mixture, while monticellite and diopside were dominant in the equivalent oxide mixture (MCS-11). Xonotlite was relatively ubiquitous throughout the range of cement mixtures; chrysotile was most prominent in the silica-poor mixtures (MCS-1) and decreased as SiO_2 increased; both phases remained after long time reactions, ~98 days. Mixtures cured in noble metal tubes, which contained carbonate produced crystallized calcite above 350°C and scawtite below 350°C over the pressure range studied. Talc increased with SiO_2 content, complementing the decrease of chrysotile.

Figure 4, an infrared spectrum of diopside-rich cured sample, shows that very little of the CO_3^{2-} appears in the final product after curing at 400°C and 68.9 MPa (10,000 psi) for 63 days. This sample without scawtite and with a very minor amount of calcite present represents one of the highest strength mixtures (see microhardness data in Table 7 [Section V]).

The oxide mixtures, on the other hand, in 7-day runs were dominated by diopside and talc, both of which increased with silica content. Xonotlite played a minor role but increased slightly as SiO_2 increased. Unreacted quartz appears in mixtures MCS-14, the most silica-rich mixture investigated, and in small amounts in some of the others.

Figure 4. Infrared Spectra of Sample 19-J-400-63-0.45

A modified calcined (1000°C for 2 hrs.) Class J cement mixture (MCS-6, and MCS-22 through 25) had only a minor amount of calcite and chrysotile in the silica poor mixtures. On the other hand, the amounts of both xonotlite and talc were inversely proportional to the SiO_2 content.

It is possible that structural and kinetic factors controlled these early stage reaction products. The hydration of $\beta\text{-C}_2\text{S}$ in Class J cement, MCS-1 through -5 (plus quartz), generated xonotlite, while the corresponding oxides (CaO , MgO , SiO_2), in MCS-11 through -15 formed diopside and talc more readily; 63- and 96-day cured mixtures with cements as starting material still contain mixtures of xonotlite, diopside, and chrysotile (Table 4).

The major difference between the run products with oxides vs. those with cement starting materials were that (1) scawtite was absent from the oxide runs and (2) diopside rather than xonotlite dominated the oxide runs, from higher-silica compositions. The latter observation seemed once again to indicate the effect of structural control and kinetics. Either xonotlite (+ chrysotile) or diopside (+ H_2O + monticillite) was the metastable intermediate phase assemblage at 400°C. In previous long-term runs with similar mixtures, all three phases were still present after 96 to 98 days of hydration in mixtures nearest the diopside composition. Because of the fine-grain size and reactivity of the oxides, diopside appears to form preferentially.

(c) Saturated NaCl: 300°C Curing. The products of mixtures prepared from Class J cement with brine used as the mixing water have a constant amount of NaCl throughout. Scawtite was no longer the dominant silicate phase, but was present at most in trace amounts. Xonotlite, the major phase in lower-silica mixtures, and scawtite now both decreased slightly as the silica content increased. Chrysotile was major only in the most silica poor mixture (MCS-1). It decreased and disappeared with increasing silica content and was gradually replaced by increasing amounts of talc. Diopside was relatively minor but nearly constant throughout. Unreacted quartz once again increased in the silica-rich mixtures.

In run products from either type of starting material, the contents of talc and chrysotile phases varied with SiO_2 content as expected. Talc increased and chrysotile decreased with increasing silica content. NaCl was fairly constant throughout, which suggests that it does not react extensively to form any new compounds. Xonotlite and diopside both decrease with increasing

silica content, as expected. Diopside is absent in the MCS-11 (1) mixture, predominant in MCS-15 (5), and then decreases from MCS-12 to -14.

The greatest differences among these product phases (comparing oxide mixes and cement mixes) are the absence of scawtite in the oxide mixtures, and the relatively minor role of diopside in the cement mixtures compared to a major presence in the corresponding oxide mixtures (the latter in runs up to 7 days).

(d) Saturated NaCl: 400°C Curing. Diopside, talc, quartz, and NaCl dominated the phase assemblages present from oxide-based mixtures. Talc and unreacted quartz increased as the mixtures became more silica rich. Talc became predominant in the MCS-12 to -14 mixtures, while diopside decreased slightly as the mixture became silica rich. Monticellite appeared only in MCS-11, which is the most silica-poor mixture, while NaCl remained fairly constant throughout. Xonotlite was relatively minor. The lack of xonotlite in these mixtures (oxides and NaCl as brine, 7-day runs) suggests that the assemblage xonotlite + chrysotile may be a metastable intermediate phase assemblage at 400°C and 68.9 MPa and would eventually be replaced by diopside (+ H₂O).

Contrasted with the oxide mixtures, the results of cement-based mixtures show some differences. For example, in cement-based mixtures, diopside occurred predominantly in mixtures MCS-1 and -5; xonotlite predominated in mixtures MCS-2, -3 and -4. Xonotlite and chrysotile remained in 63-day runs. Monticellite again appeared only in MCS-1 (in 7-day runs) and talc increased as the mixtures become more silica rich, reaching its maximum in mixtures MCS-2 and -3. The results regarding the assemblage, diopside-monticellite, are inconclusive; possibly NaCl affects the equilibria. A possibility is that at lower temperatures there is a kinetic barrier to the development of diopside, with xonotlite + chrysotile crystallizing as an intermediary; however, the latter assemblage remains even after 63 days at 400°C and 68.9 MPa.

The Class J cement-based primary reaction is

An alternative reaction from slightly different compositions, and probably stable at the highest temperatures,

The structural control of $\beta\text{-Ca}_2\text{SiO}_4$ may, in some manner which is not obvious, favor the former reaction as an intermediate even at the higher temperatures, from the diopside stoichiometric composition.

III. PROPERTIES OF CEMENT SLURRIES

A. Equipment

Physical properties of fresh cement slurries (including pumpability) are complex and important in the cementing of geothermal wells. For analysis of the properties of fresh cement slurries it is considered effective to use a co-axial rotational viscometer for some of the characteristic measurements.

Both a Brookfield Rheolog model 5X HBT and a Haake Rotovisco RV-3 Viscometer have been put into operation and utilized. The output (in millivolts) is proportional to the shear stress for both instruments. The Brookfield was calibrated with Newtonian fluids for viscosities of approximately 200 to 17,000 cP at room temperature. There was no hysteresis effect with the Newtonian fluids. In addition, the fluids produced constant viscous shear over time. The Haake Viscometer is equipped with a constant temperature circulator and two rotor sensor systems, SV-I and SV-IIP. The sensor system SV-IIP has been designed especially for cement-type fluid measurements. A phenomenon called "cracking" occurs when the distance between the rotor and the housing is too large for the range in viscosity values. The serrated edges help to prevent this from happening. For comparisons between the viscosity measurements taken from the Haake to be comparable, the apparent viscosity values must always be recorded at a particular shear rate, and upon the same part of the cycle. Measurements here were made with increasing rotor speeds. At present the rotor speeds are set for a maximum of 724 rpm. Two measuring heads have also been provided: MK50 and MK500, the latter for viscosities an order of magnitude greater.

B. Mixing Procedures

The pastes and slurries were prepared by mixing the cement with water or a solution of water and a soluble admixture. The quantity of solids, cement plus a reactive compound, used was 100g; the w/s ratio was 0.45. After the dry ingredients were stirred completely, the measurement time started when the solution was added to the cement. The paste was stirred, by hand, for 2 minutes, then, following the API standard procedure, mixed in a Waring Blender at 3500 rpm for 15 seconds and 9000 rpm for 35 seconds. An initial reading (at 6.5 minutes) was made on this mixture, which

was inserted into the pre-heated Haake measuring cup. The remaining paste was paddle-stirred using a Brookfield rotational viscometer. A new sample was taken from the paddle-stirred slurry for each of the 30-minute, 1-hour, 2-hour measurements. The viscosity has been measured up to 60°C within the Haake; the paddle-stirred mixture was kept either at room temperature ($\sim 25^{\circ}\text{C}$, $\sim 70^{\circ}\text{F}$) or at the Haake testing temperature, 15°, 25°, 35°, or 60°C.

C. Viscosity Measurements

1. Modified Aluminous Cements. Initial experiments using the Brookfield viscometer showed that the modified aluminous cements required a retarder in order to have workability necessary for geothermal well emplacement. Of the admixtures used, a lignosulfonate-type retarder was found to be the most effective in reducing viscosity, while the superplasticizer admixtures were not as effective. The identification of the interrelationships between the retarding additive and the two different calcium aluminate cements showed that there is a significant difference in the behavior of the two cements using a lignosulfonate retarder. As expected, an increasing quantity of lignosulfonate decreased the viscosity of the mixture in all comparable situations. However, brand R cement required more retarding additive than the brand S aluminous cement when viscosity was measured on the Brookfield model 5X HBT with a w/s = 0.50.

Using the Haake Rotoviscometer, the viscosity of the modified aluminous brand S cement slurry with 0.5 percent lignosulfonate additive was mixed according to the standard ASTM-C305 mixing procedure. The slurry viscosity was very irregular and appeared to have small aggregated particles within the mixture to account for the choppy behavior. The viscosity of the slurry was approximately constant at 700 cP as the rotor speeds were decreasing. The comparison between shear stress-shear rate relationships measured on slurries prepared by the ASTM and the API mixing procedures on the mixture shown in Figure 5 showed no "apparent hysteresis" in the slurry when the high-speed API mixing procedure was used at room temperature. Apparent viscosities varied for the latter mixing procedure: 800 cP @ 100 rpm (700 cP, or 7 Beardon units of consistency (BC) @ 150 rpm), 600 cP @ 200 rpm, 525 cP @ 300 rpm, and 450 cP @ 600 rpm rather than the constant values measured previously. After one hour

Figure 5. Comparison of Viscosity Values Using the ASTM and the API Mixing Procedures for a Modified Brand S Aluminous Cement

the apparent viscosity at 150 rpm was approximately 1450 cP, well within the 2500 cP limit set for the pumpable mixture.

The aluminous cement (S-2) was retarded with 0.5 to 5% lignosulfonate, and up to 2% boric acid. Early high temperature curing (60°C in the paddle-stirred slurry) increased the shear stress by a factor of two at the same admixture concentration compared with room temperature curing of the paddle-stirred slurry. Whereas the viscosity for the modified aluminous cement decreased uniformly with increasing amount of lignosulfonate retarder, this was not true when measurements were taken on the Haake at elevated temperatures (60°C). Only minor changes in viscosity occurred up to 2% admixture concentrations. However, a significant increase in shear stress occurred when the admixture concentration went from 2 to 2.5%. Apparently, lignosulfonate concentrations should be kept at or below the 2% level. Pressurized consistometer measurements have not yet been made; however, additional viscosity measurements at higher temperatures are reported in Figure 6.

2. CaO-MgO-SiO₂ System

a. Class J Oil Well Cement + MgO and Al₂O₃. For comparison, a Class J oil well cement was modified by the addition of Al₂O₃ and MgO in 10 and 20 percent quantities. An increase from 10 to 20 percent Al₂O₃ reduced the viscosity, whereas an increase of 10 to 20 percent MgO increased the viscosity of the slurry when measured on the Bookfield viscometer.

Figure 6. Comparisons of Viscosity Values for Aluminous Cement (S-2) using 27°C and 60°C Initial Mixing Temperatures

b. Class J + Calcined Chrysotile. Measurements of room temperature viscosities of some slurries ranged from a minimum of 170 cP at 600 rpm shear rate to 2040 cP (20 BC) at 100 rpm, measured with the Haake RV-3 viscometer. Viscosities of Class J cement mixed with a more coarse-grained calcined chrysotile were very much lower than when the cement was mixed with a finer-grained meta-chrysotile at a w/s = 0.45. The surface area of the former meta-chrysotile was approximately 5 m²/g; for the latter, the surface area was approximately 30 m²/g. As expected, the coarser materials consistently have had much lower viscosity values.

It appears that some workable mixes are among the new compositions. Additional detailed studies on a variety of compositions have been extended to elevated temperatures. Dowell personnel have measured the consistency of an 80% (J-2) cement + 20% calcined chrysotile (B20) + D-28 retarder (A6) + a

defoaming agent, up to a final temperature of 350°F (177°C) and pressure of 5300 psi. At a temperature gradient of 1.7°F/min and heating rate of 6.7°F/min the cement paste was pumpable for up to 240 minutes until setting started and 277 minutes for a thick set. The calibration for these data on a w/s = 0.45 paste is:

12 volts = 100 units of consistency;
8.5 v = 70 units of consistency;
3.9 v = 50 units of consistency;
1.7 v = 10 units of consistency.

IV. PERMEABILITY

A. Equipment

1. Gas Permeability Cell. Gas permeability measurements were made using a single medium-pressure cell or three such cells manifolded together. The design was adapted from an initial model of Franzen (1964), having gone through several modifications (see Figure 7). This system utilizes a commercial pressurized nitrogen tank and regulator as a source of stable nitrogen gas which can be varied from 0.1 to 5.5 MPa (14.7 to 800 psi). The measuring cells for this system are made from 75-mm-diameter brass, internally threaded to accept brass screw plungers, which are fitted with neoprene O-rings. The O-rings directly seal the top and bottom of the sample. The cells are designed to accept 25.4-mm-diameter samples up to 50 mm thick. The gas which has passed through the sample is measured by the amount of water displaced in a calibrated cylinder. A small vent hole drilled through the middle of the cell wall allows any gas escaping around the O-ring seal from the high pressure side to exit the sample chamber and to reduce the possibility of its entering the gas stream that has passed through the sample, thus giving a false higher intrinsic permeability measurement.

2. Water Permeability Cell. Four water permeability cells have been constructed; two have a 500 ml capacity, two have a 1000-ml capacity (see Figure 8). The two larger cells and one of the 500-ml cells were constructed

Figure 7. Schematic Diagram (above) of the Gas Medium Pressure Permeability Apparatus (below). Stippled Areas in Diagram Represent Water in the System

Figure 8. Schematic Diagram (above) of the Water Permeability Apparatus (below). Stippled Areas in Diagram Represent Water in the System

of a miscellaneous grade of 300 austinitic stainless steel; the fourth cell was constructed of Incaloy, to be both Mg and Cl resistant. All four have an upper pressure limit of 34.5 MPa (5000 psi) with a safety factor of 4. At present, three cells are connected to Soltec Model 3314 strip chart recorders with calibrated load cells on top of which are fitted plastic collecting bottles. As the water permeates the sample, it drips into the plastic bottle.

3. Hoek-Franklin Cell. Some testing was done on the Hoek-Franklin Permeability Cell which allowed for lateral confining pressures of up to 34.5 MPa (5000 psi) while measuring nitrogen gas flow through the sample. The outer surface of the sample had to be defect free. The permeability for a modified aluminous cement sample was 1.9×10^{-4} darcys with a confining pressure of 27.6 MPa (see Figure 9). As the confining pressure was reduced to 10.3 MPa (1500 psi), the permeability increased.

B. Permeability of Cured Sample

Two approaches have been used to measure permeability. Klinkenberg (1941) demonstrated that gas permeability values plotted as a function of reciprocal pressure could be extrapolated to infinite pressure resulting in a permeability value equivalent to that obtained with a non-compressible liquid. With this approach, it was found that permeability values using nitrogen gas at pressures up to 5.5 MPa (800 psi) resulted in permeabilities for the aforementioned cement samples which were all less than the 0.1-millidarcy upper limit set for this contract. Agreement of extrapolated permeability values with actual values obtained using water were quite good, considering the fact that the gas dehydrated the sample whereas the water hydrated the sample during the course of a measurement. A comparison of the two permeability values obtained for a few samples is given in Figure 10. In most cases, the water permeability was an order of magnitude less than the extrapolated fluid value.

Samples prepared with the calcined chrysotile* and cured for 24 hours had both a low extrapolated fluid permeability, and

*Chrysotile (asbestos) was heat treated at 650°C for 1 hour, then put into a ball mill to break into smaller particles. Phases present include amorphous material and some forsterite as determined by x-ray diffractometry.

Figure 9. Comparison of Permeability Between the Modified Class J and Modified Aluminous Cement Samples. Note the Hoek-Franklin vs Medium Pressure Cell Permeability of HYD-2 are 1.85×10^{-4} and 1.20×10^{-2} Darcys, Respectively

Figure 10. Water Permeability Curves for Five Cement Composites: (3) Type III 0.3 w/c (salt-sat. mixing water) Cement Paste Cured at 25°C for 60 days; (4B) Similarly Prepared and Cured Type I Cement Paste; (2B-V-60-60) Similarly Prepared (without salt) Type V Paste Cured at 60°C; (4) Type III 0.4 w/c (solid) Seeded Cement Composite with Added 5 μ m quartz; 1.0 CaO:SiO₂ Ratio Cured at 25°C For 60 Days. (2B-V-60-28-1-IT) Type V Cement Composite as in (4) but Cured at 60° for 28 Days

a low water permeability (see Figure 11 and Table 6). Pressurized nitrogen gas was forced through the sample three hours after drying at 110°C (6.5×10^{-7} darcys) and then after 19 days of drying at 110°C (1.2×10^{-6} darcys). Water was forced through the sample at 10.3 MPa (1500 psi); approximately the same permeability value was determined. After an identical sample was cured first in water and then in a 20 percent NaCl solution, the gas permeability was extremely low (10^{-9} darcys) and the water permeability was approximately 10^{-4} darcys. The 24-hour sample far exceeds the criteria set at the beginning of this study of less than 0.1-millidarcy permeability to water. A modified oil well cement (w/s ratio = 0.45) cured for 24 hours in deionized water at 400°C had an extrapolated water permeability of 6.5×10^{-7} darcys. A water permeability for this sample 3/8-in-thick by 1-in-diameter slice resulted in a permeability of 4.9×10^{-7} darcys. A similar sample cured for seven additional days in a 20% brine solution had an extrapolated fluid permeability of 8×10^{-9} darcys and a water permeability of approximately 10^{-4} darcys when deionized water was forced through the sample for one hour. It was hypothesized that soluble solids from the initial brine within the pores were dissolving with the passage of water through the sample. Had a brine solution been used as the permeating fluid, this might not have been the case.

C. Permeability of Rock Materials

Figure 12 illustrates the water permeability of a Tuscarora quartzite rock sample which was used in the cement-rock bonding study described in a later section. Permeability is almost independent of pressure and an extrapolated value results in a permeability of approximately 7.3×10^{-6} darcys.

V. STRENGTH PROPERTIES OF THE CURED SAMPLES

A. Compressive Strength

Prior to compressive strength testing of a cured sample, the ends were sawed with a water-cooled diamond saw, then lightly polished by sanding and

Figure 11. Permeability Measurements Made with Nitrogen Gas
Pressurized up to 5.5 MPa (800 psi)

Table 6

Typical Property Measurements for a Class J Cement
Mixed with Calcined Chrysotile
(Composition shown as Q in Figure 2)

sample number	790002	790003	790036
curing conditions	236°C; 1-day deionized water	236°C; 1-day deionized water. Room temp to operating temperature time = total of 2 days. 236°C; 7 days. 20% NaCl solution.	400°C; 206 days deionized water.
w/s; w/c	0.39; 0.63	0.39; 0.63	0.78; 0.47
bond strength	4 MPa (575 psi)	7 MPa (1025 psi)	0.6 MPa (90 psi)
permeability:			
nitrogen gas extrapolation (darcys)	6.5×10^{-7} (3 hours' drying) (1.2×10^{-6}) (19 days' drying)	8.0×10^{-9}	--
pressurized water (darcys)	5.0×10^{-7}	1.0×10^{-4}	
phases present: (XRD)	forsterite quartz (unreacted) calcite tr β -C ₂ S	scawtite NaCl forsterite	diopside

Figure 12. Water Permeability of Tuscarora Quartzite Core

returned to a curing solution of Ca(OH)_2 . The samples were blotted dry just before testing. A square of paper was placed between each end of the sample and the machine platens to fill any voids in the surface of the sample and to protect the equipment. A Tinius Olsen Testing Machine was used to measure the compressive strength with a loading rate of 0.025 inches (0.05 mm) per minute.

The compressive strength for a hardened modified calcium aluminate cement slurry cured at 400°C and 9.6 MPa (1400 psi) for 60 and 156 hours had a strength of 29.4 MPa (w/s = 0.4). See Table 7. The compressive strength for a modified Class J oil well cement after curing for 24 hours was increased after additional curing in a 20 percent NaCl solution for 7 more days. The 10-day compressive strength was 12.2 MPa (1775 psi). Both modified cured cement slurried meet the compressive strength requirements set.

B. Microhardness

Since many samples were small and did not lend themselves to conventional compressive strength measurements, an attempt was made to correlate microhardness versus compressive strength on some larger specimens. These data are summarized in Table 7 and Figure 13. It is seen that microhardness measurements on such fine-grained homogeneous materials can be used, as a first approximation, as an indicator of strength.

Samples were cut to make the ends parallel with the samples approximately 1 cm thick. The samples were then ground using a #3 (3 micrometer) alumina powder and water on a flat ground-glass surface. The surface of the sample was optically polished using 1-micron-sized diamond paste until enough surface area was present to make the microhardness tests. At first, polishing was done in a nitrogen atmosphere to reduce sample reaction, but this was found to be unnecessary.

A Leitz miniload microhardness tester with a 40X objective was used to test the hardness of the cured samples. Twenty measurements were made with the Vickers indenter for each sample. The highest and lowest values were omitted and a mean and standard deviation were calculated and reported for each sample as representing the hardness (strength) of the sample.

A new technique for polishing cured samples using a Buehler polisher prior to microhardness testing was initiated. The technique is summarized below.

Table 7
Compressive Strength and Microhardness Measurements for
Modified Calcium Aluminate and Class J Oil Well Cement Samples
With a w/s = 0.45

Sample	Curing time (days)	Starting material	Compressive strength* kg/cm ²	Microhardness kg/mm ²
<u>Deionized water as mixing water</u>				
*A (Fig. 1)		R + Min	82	soft
*C (Fig. 2)		R + Min	127	--
*D (Fig. 1)		S + 5% P + Min	142	16.7 ± 4.3
*E (Fig. 1)	2.5	S + Min	311	30.66 ± 11.5
*HYD-2	6.5	S + Min	306	17.02 ± 5.5
*F (Fig. 1)		R + Min	227	25.8 ± 10.9
*G (Fig. 1)		S + 5% P + Min	144	21.6 ± 7.8
*R (Fig. 1)		R	576	48.4 ± 9.3
*19-J-400-3 (Fig. 2)		J + Min + MgO	-	25.0
*5-J-400	10.0	90% J + 10% MgO	341	19.17
*6-J-400		67% J + 23% Min + 10% MgO	203	13.04 ± 3.3
*6H-J-400		67% J + 23% Min + 10% MgO	163	10.82 ± 1.1
*18-J-400-96 (Fig. 2)		J + MgO	169	21.10 ± 2.1
*HYD-21		S + Min	576	50 ± 9.6
*HYD-15			94	
6T-J-400	26	67% S + 23% Tripoli		5.09 (0.71)
6-J-400	26	67% S + 23% Min		10.82 ± (1.1)
6-J-400	>26	67% S + 23% Min	203	13.04 (3.3)
8-J-400	26	44% J + 46% Min + 10% MgO		8.51 (0.77)
8T-J-400	26	44% J + 46% T + 10% MgO		too soft
18-J-400	36	J + 15% MgO		18.49 (1.03)
18-J-400	63	J + 15% MgO		29.71 (4.28)
18-J-400	96	J + 15% MgO	169	21.10 (2.1)
19-J-400	36	J + 10% Min + 20% MgO		26.34 (2.04)
19-J-400	63	J + Min		35.07 (3.70)
19T-J-400	36	J + 10% Tripoli + 20% MgO		15.88 (1.45)
19T-J-400	63	J + 10% T + 20% MgO		18.41 (2.63)
20-J-400	36	J + 10% MgO + 4% CaO		18.25 (1.91)
20-J-400	63	J + 10% MgO + 4% CaO		17.32 (0.99)
*19-J-400 (790037)	206	J + calcined chrysotile 999		21.12 (1.32)
<u>Saturated brine as mixing water</u>				
5N-J-400		90% J + 10% MgO		5
5N-J-300		90% J + 10% MgO		5
18N-J-400		85% J + 15% MgO		18
18N-J-300		85% J + 15% MgO		18
19N-J-400		70% J + 20% MgO + 10% SiO ₂		19
19N-J-300		70% J + 20% MgO + 10% SiO ₂		19

*Samples were cured in large (500 cc) autoclave if compressive strength measurements are given.

Figure 13. Comparison Between Compressive Strength and Microhardness Values for Hydrothermally Cured Samples

(1) All specimens were cleaned ultrasonically between each polishing step. This was most important for cement samples since numerous single pores are capable of holding and transferring the polishing compound from one stage of polishing to another, thereby destroying the polish.

(2) The weight on the Buehler 69-1000 Minimet polisher/grinder polishing arm was reduced to approximately 277g (0.5 pound). Minimizing the load inhibits plucking of the coarser size fractions.

(3) Diamond paste was found to be the superior polishing agent (with oil lubricant). To obtain a uniform mat surface for each size, polishing time for each polishing step (10-, 3-, 1-, and 0.25- mm-sized diamond paste) was approximately 5 minutes (Al_2O_3 should not be used as a polishing or buffing compound because it tends to produce greater relief).

Microhardness measurements, were made with the Vickers Miniload Hardness Tester after polishing with the new system versus the "old" hand technique. Both techniques produced the same mean value of 50 kg/cm² for a hydrothermally cured modified aluminous cement. The standard deviation, however, decreased from 10 for the "old" technique to 3 for the new technique. This may have been due to unequal lengths of the diagonals of the indentations

using the "old" method. The equal diagonal indentations gave reproducible results ($\pm 2.5\%$). The shape of the diamond indentation varied considerably using the "old" method. When the diagonals were unequal, crushing and gouging of the surrounding surface area were observed and the diamond shape was distorted. Both the average of the perfect diamond indentations and the frequency of the poorly formed indentations should be reported and compared. Static indentation tests should be used in conjunction with scratch hardness tests to look at the relative hardness over larger areas. It is concluded that a well polished surface is required to make meaningful measurements.

The comparison between compressive strength and microhardness measurements given in Table 7 shows that the microhardness value is larger than the compressive strength by a factor 5 to 15. It appears that microhardness is a valuable technique for small samples of relatively homogeneous materials.

When a comparison was made between modified Class J oil well cement samples mixed with water, and those mixed with a brine, the former were nearly twice as strong as those mixed with the brine (see Table 7 and Figure 14). On the basis of these microhardness measurements, composition #19 with 20 percent MgO near the xonotlite-chrysotile join was chosen as the composition with the highest probability of having favorable cementing properties (see Figure 14). Samples made with tripoli or perlite as the source of SiO_2 , having much higher w/c ratios, had much lower microhardness values. The lighter-weight ingredients were tested to reduce the weight of the final emplaced column.

C. Bond Strength

Once it became apparent that cements within the C-A-S-H system and the C-M-S-H system held promise, they were evaluated in terms of their bond strength to rock and to steel in various states of degradation. All bond strength measurements were made on the composition (in the C-A-S-H system) 13% CaO, 37% Al_2O_3 , 50% SiO_2 (50:50 brand S cement + 5 μm Min-U-sil). In the C-M-S-H system the composition was 28% CaO, 20% MgO, 52% SiO_2 shown as mixture #19 throughout this study. The water/solid ratio of 0.45 was constant for all slurry bond strength measurements.

1. Cement/Rock Bonding. Bond strength to a high-SiO₂ rock, the Tuscarora quartzite, was measured as a function of time. Five cm outer-diameter rock cylinders having a 1.9 cm inner diameter were cored from 3.8-cm-thick slabs of Tuscarora quartzite using diamond core drills cooled with water (see Figure 15). These cylinders were then filled with the cement slurries under investigation and allowed to cure at 400°C and 34.5 MPa (5000 psi). A punch and die (Figure 16) was designed to measure the force required to break the bond between the central cement core and the host rock. The bond strength was calculated as that force over the surface area of the cured cement sample cylinder. Data collected using two methods of sample preparation are illustrated in Figure 17. Half-filled circles represent samples which were cut in half just prior to the push-out testing, while solid circles represent those samples which were not cut in half.

The calcium aluminate cement samples cured for 14 days within the same pressure vessel illustrate that the bond strengths for samples cut in half were markedly lower [strength almost 0.7 MPa (100 psi)], but reproducible as compared with the sample not cut in half [almost 2.8 MPa (400 psi)]. It appears that end effects were introduced by cutting the sample. This was verified by optical examination of some of the sliced surfaces. Pitting of the interfacial region between the rock and the cement sample was observed. This led to the conclusion that samples should be tested with no precutting. However, since these experiments are very time consuming and there was not sufficient time to reproduce earlier experiments, both types of data are reported here. No trends are evident here, but it is possible to report that the bond strength between the sample and the host rock was greater than 0.7 MPa (100 psi) and may be as great as 2.8 MPa (400 psi) for samples which were undisturbed before the push-out test. Runs of longer duration (~6-7 months) were under way, during the first writing of this report. These data are reported in Figure 17. Bonding appeared to be physical in nature. The interface between the cement and the rock was distinct and sharp (see Figure 18).

Near the end of the study a new lot of the brand S high alumina cement was utilized. Bonding between the host rock and the "new" cement was on the order of 3.5 MPa (500 psi) on specimens prepared using the ASTM mixing procedure outlined in the viscosity section. Bonding between the rock and the fresh material using the API mixing procedure was approximately 2.1 MPa (300 psi).

Figure 14. Microhardness Measurements for Modified Class J Cement Samples Hydrothermally Cured at 300°C, 68.9 MPa (10,000 psi) for 36, 63, and 96 Days

Figure 15. Tuscarora Quartzite Rock Cores used for Cement/Rock Bond Strength Measurements

Figure 16. Punch and Die Assembly Used for Bond Strength Measurements

Figure 17. Bond Strength Measurements: Cement/Rock in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ Systems

Figure 18. Bonding Interface Between Cement and Rock

Both samples of the fresh material were cured for 14 days at 400°C at 34.5 MPa (5000 psi), showing a very large bond strength relative to the "old" cement. The test specimens all consisted of a 50:50 mixture, by weight, of the aluminous cement combined with 5-micrometer quartz, and a retarder 0.5 percent lignosulfonate mixed with deionized water for a $w/s = 0.45$. The new cement, as

shown in Appendix G, had less alumina and it was a fresh batch. These are possible explanations for the differences obtained. Previous measurements (Roy, 1976) had been made between class J cement (J-1) and both Juniata sandstone and Valentine limestone. These strengths were very similar thus we have concentrated our studies on Tuscarora quartzite, a purer quartz rock.

After curing the Class J oil well cement slurries in the Tuscarora quartzite cores, the host rock was blackened (reduced state of iron in the rock?) rather than being a pure pink-white rock. The contact between the aluminous cement and the rock was distinct, while a blackened ring was present between the host rock and the cured cement slurry for all tests with the Class J oil well cement. The element distribution done by a scanning electron microscopic analysis of the blackened ring showed decreasing amounts of calcium and silica as one transversed the cement sample to the edge of the host rock (see Appendix I), but no significant changes in other components.

2. Cement/Steel Bonding. Values for bond strength to steel were also measured and are shown in Figure 19. Mixtures of cement slurries were placed in thin-walled steel cylinders fitted with a 1.9 cm central core of common steel rod (see Figure 20). The steel was cut to size and cleaned. Some samples were cleaned in acetone, others were ultrasonically cleaned in a laboratory soap solution. Two types of steel rod were used. The steel material was rusted to simulate rusted casing or it was used in its original unoxidized condition. All tests were made at 400°C, and 34.5 MPa (5000 psi) for seven days. Since sample geometry was such that the steel rod protruded from the ends of the cement cylinder, it was an easy matter to push the rod from the cement using the previously mentioned punch and die. As shown in Figure 18 the bond strength to the two forms of steel for the two types of cements was always greater than 0.7 MPa (100 psi). Additional trends are difficult to interpret. As a class of cements, it seems that the C-M-S-H cement has a higher bond strength to the unoxidized steel than does its C-A-S-H counterpart. When it comes to bonding to rusty steel the rust appears to act as a lubricant; it flakes to break away, allowing the steel rod to move at about 0.7 to 1.4 MPa (100 to 200 psi).

It is concluded that both cement types meet the minimum requirements for bond strength as set forward in the original contract. Both cements show promise and should still undergo additional testing.

Figure 19. Cement/Steel Rod Bond Strength (400°C , ~ 345 MPa) vs Condition of Steel Rod Before 7-Day Hydration in the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (below) Systems

Figure 20. Steel Cylinder and Rod for Cement/Steel Bond Strength Measurements

VI. DISCUSSION AND CONCLUSIONS

The objective of this study was to develop cement formulations that could withstand high temperatures, high pressures, and corrosive geothermal environments. A large number of compositions modified from conventional cements have been studied for their potential as geothermal cementing materials. The most feasible compositions appear to be those derived from mixing calcined chrysotile or other magnesian phase with Class J cements; or from adding quartz flour to calcium aluminate cements, with minor additions of other components, to achieve optimal compositional adjustments and adequate mixing properties.

Major emphasis has been given to determining phase constitution of the hydrothermal reaction products at temperatures up to 400°C and 68.9 MPa (10,000 psi) for periods of time ranging from 1 day to 6 months. For this purpose, not only modified commercial cements but mixed oxide compositions and other raw materials were utilized to provide comparisons. The goal of the latter experiments was to determine the final equilibrium reaction products, or, barring achievement of full equilibrium, to determine whether or not the phase changes taking place with increasing reaction time would be likely to result in deterioration of the cements.

From within the two basic compositional systems $\text{CaO-MgO-SiO}_2\text{-(H}_2\text{O)}$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(H}_2\text{O)}$ (neglecting minor amounts of additional components), ranges of cementing compositions have been established, and selected optimized cements have been thoroughly investigated. Thus, two new potential geothermal cements, each affording some range in composition and potential source materials, have been proposed and tested for phase compatibility, mechanical properties (including bonding to steel and rock), permeability, and resistance to brine corrosion; microstructural characteristics were investigated; and other characterization studies were made. Viscometric properties were determined at lower temperatures and atmospheric pressure, and were followed by consistometer measurements made at Dowell Co. at elevated temperature and pressure. An 80/20 mixture J-2 cement/calcined chrysotile mixture has been shown as pumpable.

The properties of the selected cements were found to exceed the minimum requirements having adequate phase and microstructural stabilities when reacted for prolonged periods at high temperatures and pressures, strengths ranging from 15 to 55 MPa, well above the minimum requirements, adequate bonding to steel and

selected rock, and permeability which remained low after curing under geothermal conditions for 24 hours to 98 days, and in some experiments when exposed to NaCl-rich brines. The basic formulations for these two optimum cements were compositionally near 50 percent SiO_2 mixed with either high-alumina cement (brand S) or a Class J oil well cement. The former cement product contains substantial amounts of the anhydrous phase hexagonal anorthite, whereas the latter contains mixtures of xonotlite, chrysotile, and the anhydrous phase diopside. No significant deterioration was noted in the latter cements upon formation of the anhydrous mineral, diopside. The use of different forms of silica controlled the reactivity with the less reactive constituents producing a stronger cured final cement product, usually because of lower w/s ratios used.

The presence of the anhydrous phase hexagonal anorthite in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (C-A-S-H) system and diopside in the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ (C-M-S-H) system were correlated with satisfactory strength properties. Materials-dominated structural and kinetic factors were involved in controlling the early stage reaction products. Mixtures of silica-poor high-alumina cements in the C-A-S-H system mixed with quartz produced hexagonal anorthite, a major component of a cementitious product, whereas structural control was apparently effective when other starting materials were compositionally adjusted to the same anorthite stability field, e.g., oxides, $\beta\text{-C}_2\text{S}$, producing instead the triclinic polymorph of anorthite, an apparently noncementing material. A saturated NaCl solution used as the mixing water accelerated the reactions generally, resulting in the formation of some diopside in the C-M-S-H system at a curing temperature of 300°C . In both the cement and oxide mixtures cured at 400°C , diopside predominated in the silica-poor mixtures whereas xonotlite predominated in the silica-rich mixtures. However, xonotlite and chrysotile were present with diopside as a three-phase assemblage (+ calcite, due to CO_2 contamination) in appropriate mixtures even after 63 days' curing. In the latter case, fibrous or lath-like structures dominated the microstructures, a condition apparently related to the cementing properties. Intergrown microstructures apparently serve to enhance the strength.

During this report writing period cement/rock bond strength evaluations of cementing compositions cured for more than six months at 400°C and elevated pressure were measured. In addition, setting times and viscosity measurements on several modified aluminous cement compositions were made at elevated

temperatures. Experiments carried out at room temperature indicate that the modified cements are workable and pumpable for up to three hours. Experiments carried out at 177°C indicate that modified C-M-S cements are workable and pumpable for up to four hours with a 0.3% retarder added. Results of other recent research on the effects of alkalis are summarized in Appendix H, where it is shown that compositions in the C-M-S system are relatively little affected.

APPENDIX A

CALIBRATION OF AUTOCLAVES

Autoclaves used in the experimental program were of two types: the small, 300-ml, conventional test-tube or Tuttle cold-seal and a large Barnes 500-ml autoclave (modified from the Barnes-Rocking assembly). The conventional 30-ml vessels were externally heated in Kanthal wound furnace assemblies. During the first year of this study, heating curves were derived for the furnaces used to heat the larger 500 cc vessels (50% of vessel in furnace). A temperature comparison between the inside bottom, outside bottom, and outside two inches above the bottom are shown in Figure A-1. At an equilibrium temperature of 600°C there was a temperature differential of 120°C between inside and outside and 30°C between the bottom and 2 inches above the bottom (outside). As the furnace temperature setting increased, the difference between the inside and outside temperatures also increased as shown in Figure A-2. However, the temperature differential between inside and outside was reduced to less than 50°C with new furnace design (6-inch i.d., 12-inch height). This reduction was possible because the entire autoclave could now be placed in the furnace for a more uniform temperature distribution. The new furnaces were fabricated from Thermcraft, Inc. The heating elements can withstand a maximum temperature of 1000°C (1850°F).

Figure A-1. Heating Curves for Autoclave

Figure A-2. Relationship Between Interior and Exterior Temperature for Autoclave

APPENDIX B

PRELIMINARY DATA AND SUMMARY OF PREVIOUS PHASE DATA: $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$

Previous published data for the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (Barrer and Denny, 1961, and Koizumi and Roy, 1960) for 300°C stability (Figure B-1) and for 400°C stability (Figures B-2 and -3) have been supplemented by experiments in the present study at 300°C (48 days), 400°C (10 days), and 400°C (48 days) in Figures B-4, -5, and -6 respectively. A portion of the system, at the join $\text{CaO-Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{-SiO}_2\text{-H}_2\text{O}$, had been investigated by Koizumi and Roy to determine the phase relationships for calcium zeolites as shown in Figure B-3. In addition, they studied the equilibrium relationships in the zone labeled aluminous cements to determine the stability limits and structure for a number of minerals and synthetic phases in this quaternary system. The stable phases for the 400°C cured samples are listed in Tables B-1, -2, and -3. All were oxide starting materials except for those cement starting materials listed in Table B-3. The latter run products were dominated by phase X (hexagonal anorthite), the best cementing mixtures.

Figure B-1. Summary of Previous Work in the System $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 300°C and 27.6 MPa (4000 psi) (Barrer and Denny, 1961) and at 300°C and 101 MPa (14,700 psi) (Koizumi and Roy, 1960)

Figure B-2. Summary of Previous Investigations in the System $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 400°C and Approximately 27.6 MPa (4000 psi) (after Barrer and Denny, 1961; Koizumi and Roy, 1960)

Figure B-3. Phases and Compositions of Interest in the
CaO-Al₂O₃-SiO₂-H₂O System

Figure B-5. Preliminary Compatibility Relationships Suggested from Results with Gel and Oxide Starting Mixtures in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ System Treated for 10 Days at 400°C and 68.9 MPa (10,000 psi)

Figure B-6. Preliminary Compatibility Relationships in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ System

Table B-1

Preliminary Data Using Gel Starting Materials for the System $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (Figure B-6) treated hydrothermally at 400°C and 68.9 MPa (10,000 psi) for 10 to 14 days.

Mix No.	Phase assemblages	
3	bicchulite, $\text{C}_4\text{A}_3\text{H}_3$, Al_2O_3	
8	anorthite, hibschite (hydrogarnet), minor xonotlite	
13	anorthite, hibschite, xonotlite	
12	xonotlite, hibschite, anorthite	
14	anorthite, xonotlite, truscottite	
11	xonotlite, anorthite, truscottite	
Class J Cement	xonotlite, quartz, minor truscottite (unknown)	
15	anorthite, truscottite	
6	anorthite, truscottite, quartz, wairakite	
10	truscottite, anorthite, wairakite, quartz	
1	wairakite, anorthite	
4	truscottite, wairakite, mordenite, quartz	non-equilibrium
5	anorthite, quartz, Al_2O_3 , (unknown)	non-equilibrium
7	quartz, anorthite, Al_2O_3 , xonotlite	non-equilibrium
9	anorthite, Al_2O_3 , unknown (may be xonotlite)	non-equilibrium
2	anorthite, Al_2O_3 , xonotlite	non-equilibrium

Table B-2

Preliminary Data from Reagent Grade Gel Starting Materials in the System
 $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ for Hydrothermal Curing at 300°C and 400°C,
 68.9 MPa (10,000 psi) for 48 Days

Composi- tion number	Temp (°C)	Phases obtained	Comments
1	300	not determined	
	400	wairakite + anorthite	
2	300	not determined	
	400	anorthite	
3	300	not determined	
	400	bicchulite + boehmite + $\text{C}_4\text{A}_3\text{H}_3$	
4	300	heulandite + epistilbite + truscottite	
	400	wairakite (?)	no quartz no truscottite
5	300	not determined	
	400	reaction very slow, did not react completely	
6	300	truscottite + epistilbite	
	400	anorthite + wairakite + quartz + truscottite	
7	300	not determined	
	400	reaction very slow, did not react completely	
8	300	anorthite + hexagonal anorthite + phase X (?) + hibschie + minor amounts xonotlite	
9	300	not determined	
	400	reaction very slow, did not react com- pletely	
10	300	xonotlite + minor anorthite + minor hibschite	
	400	anorthite + wairakite + truscottite	
11	300	xonotlite + truscottite	
	400	anorthite + xonotlite + unidentified phase	unidentified phase 2θ values: 15.9, 18.3, 22.7, 23.2, 26.15, 26.8
12	300	xonotlite + anorthite + hibschie	
	400	xonotlite + hibschie + anorthite	
13	300	hibschite + anorthite + phase X (?) + xonotlite	
	400	hibschite + anorthite + xonotlite	
14	300	truscottite + anorthite (?) + xonotlite	
	400	xonotlite + anorthite	
15	300	truscottite + anorthite (?)	
	400		

Table B-3
Preliminary Data from Calcium Aluminate Cement, Perlite, and Min-U-sil (quartz) Starting Materials, 400°C

Figure 1 notation	Comp. No.	Cement type	w/s	5 μ m Minusil g	Temp. °C	Perlite g	Press. psi	w/c	Time days	Wt % CaO	Wt % SiO ₂ *	Wt % Al ₂ O ₃	Phases observed with cement starting material
A	HYD-3	50 g brand R	0.80	74.34	465	50	1400		14	12.5	65	22.5	quartz + phase x + wairakite (?) + anorthite (?)
A	HYD-6	75 g	0.60	74.34	365	25	3000	1.78	21		65		quartz + phase x + wairakite + anorthite
F	HYD-4	50 g brand R	0.80	8.04	465	50	1400	1.73	14	20.0	45	36.5	quartz + phase x + anorthite (with some peaks missing)
F	HYD-8	75 g brand R	0.50	8.04	365	25	3000	0.95	21		45		phase x + wairakite + triclinic anorthite
C	HYD-5	50 g brand R	0.80	35.67	465	50	1400	2.17	14	16.0	55	29.0	quartz + anorthite + hexagonal anorthite (?)
C	HYD-7	75 g brand R	0.55	35.67	365	25 g	3000	1.28	21		55		quartz + phase x + wairakite + anorthite
E	HYD-1	50 g brand S	0.40	50	400	--	1400	0.80	60 24	14	50	44	phase x + boehmite + quartz
E	HYD-2	50 g brand S	0.40	50	400	--	1400	0.80	156 24	14	50	44	phase x + wairakite + quartz

APPENDIX C

PRELIMINARY DATA AND SUMMARY OF PREVIOUS PHASE DATA: $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$

The stable run products for mixtures (Table C-1) in the C-M-S-H system are given in Table C-2 and Figure C-1. Through these samples the location of the best cementing area was found to exist along the xonotlite-chrysotile join (mixtures #5, 20, 18, 19). Mixtures having less than 35% SiO_2 were not cementitious; mixtures containing monticellite were less strong as the amount of SiO_2 increased from composition MCS-1 to MCS-4. The strength increased through the series from 20 to 19 for runs of up to 96 days.

Table C-1

Compositions of Interest Shown in Figure C-1

	CaO	MgO	SiO ₂	wt %
(1)	33	33	33	
(2)	25	50	25	
(3)	25	25	50	
(4)	45.4	--	54.6	{ Class J Cement 90% Class J Cement 10% MgO
(5)	40.9	10	40.1	
(6)	30	10	60	
(7)	10	30	60	

Table C-2

Preliminary Data for Hydrothermally Cured Mixtures
in the System CaO-MgO-SiO₂-H₂O, 400°C, 68.9 MPa
(10,000 psi)

Composition No.	Time (days)	Phases obtained
1	7	monticellite + brucite
	21	monticellite + brucite
2	3	monticellite + brucite
	21	monticellite + brucite
3	21	monticellite + xonotlite
4	7	gyrolite + xonotlite + quartz
	21	xonotlite + quartz
5	7	xonotlite + gyrolite + quartz
	21	xonotlite + talc (trace)
6	7	gyrolite + xonotlite + quartz
	21	xonotlite + talc
7	3	xonotlite + talc
	17	xonotlite + talc
8	3	gyrolite + xonotlite + quartz
	21	xonotlite + quartz
9	7	gyrolite + xonotlite + quartz
	21	xonotlite + quartz
10	21	xonotlite + quartz
11	21	xonotlite + talc + quartz
12	7	talc + MgO + quartz
(talc)	21	talc
13	3	chrysotile (poor crystallinity)
(chrysotile)	21	chrysotile
14	3	xonotlite + gyrolite + quartz
(xonotlite)	21	xonotlite
15	7	gyrolite + xonotlite + quartz
(gyrolite)	21	xonotlite + quartz
16	7	xonotlite + monticellite (trace)
	17	xonotlite + monticellite
17	21	chrysotile + monticellite (trace)

Figure C-1. Numbered Compositions Correspond to Those Being Investigated in the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ system. Starting materials were: Gel, Oxide, and Modified Commercial Cements

APPENDIX D

PERMEABILITY

Permeability is perhaps one of the most important property measurements made on cured cement samples for geothermal well applications. Therefore, the permeability has been measured on cured samples using both pressurized nitrogen gas and pressurized water forced through 1-inch diameter samples, approximately 0.5-inch thick. Comparisons between the two measurements are discussed in the main text of this report.

Because of the high pressures [2000 psi (13.8 MPa)] used to drive water through the sample, there was some question as to the applicability of Darcy's Law which applies to laminar flow regimes only. Within the laminar flow regime, the velocity of flow is proportional to the first power of the hydraulic gradient. The Reynolds number, a dimensionless ratio of the inertial to viscous (resistive) forces, serves as a criterion to distinguish between laminar and turbulent flow regimes. This numerical concept has been applied to establish the limits of the two flow regimes. A Reynolds number of 2000 or less is the upper limit for laminar flow in pipes. For porous media flow, the upper limit for the validity of Darcy's Law is at a Reynolds number of between 1 and 10 (Todd, 1963). For a medium consisting of uniform lead shot the limiting Reynolds number was about 4 (Lindquist, 1933). Up to the critical value there is a linear relationship between the velocity of flow and the first power of the hydraulic gradient, or in other words, the viscous forces predominate over the inertial forces. The Reynolds number is expressed as

$$N_R = \frac{\rho D v}{\mu},$$

where

ρ = fluid (water) density (0.998 g/cm³ @ 20°C),

μ = viscosity of fluid (water) (1.005 cP at 20°C = 1.005×10^{-2} g/(cm-sec) @ 20°C),

v = macroscopic velocity = Q/A = volume/area,

D = characteristic length.

Recommended as the best characteristic lengths are (a) the square root of the intrinsic permeability (Todd, 1963) and (b) pore diameter of the sample.

The intrinsic permeability of a poor aquifer is on the order of 10^{-11} cm^2 (Todd, 1963); the pore size of a hardened portland cement with the highest frequency is on the order of $20 \text{ \AA}$ ($2 \times 10^{-7} \text{ cm}$) (Mikhail, Copeland, and Brunauer, 1964). Both these characteristic lengths give a flow regime within the laminar region.

Calculations for permeability with water pressurized to 2000 psi use the following formula:

$$k = \frac{\mu Q \ell}{A dP}$$

where

k = intrinsic permeability (Darcys)

μ = fluid viscosity (cP) = 1.002 cP for water at 20°C

Q = rate of flow (cc/sec) = volume/time

A = cross sectional area (cm^2)

$d\ell$ = height of specimen or thickness (cm),

dP = hydraulic driving pressure (atm) = 136.09 atm (2000 psi)
for most experiments

For all calculations a constant of 1.453×10^{-3} was derived for a driving pressure of 136.09 atm, a surface area of 5.067 cm^2 , and a viscosity of 1.002 cP at 20°C .

$$k_a = \frac{(1.002 \text{ cP})(Q)\ell}{(5.067 \text{ cm}^2)(136.09 \text{ atm})} = (1.453 \times 10^{-3})Q \ell \text{ (Darcys)}$$

Calculations for pressurized nitrogen gas forced through the samples have been programmed for both the HP-65 (on magnetic card) and TI-57 calculators using the following formula:

$$k_a = \frac{\mu h}{A} (\bar{Q}) \left(\frac{1}{\text{pressure}} \right),$$

where

k_a = apparent gas permeability (cm/sec),

μ = viscosity of nitrogen gas = 0.0176 cP,

h = thickness of sample (cm).

The pressure may be calculated using average gas pressures of (1) $\Delta P = P_2 - P_1$; (2) $\bar{P} = 1/2 (P_2 + P_1)$; or (3) $\bar{P}' = 1/2 \sum (P_2 + 1)^n$ for $n = 1, 2$. Option (3) was used with $\mu h/A = 3.455 \times 10^{-3}$ to calculate gas permeability values (1964).

Both these characteristic lengths give a flow regime within the laminar region.

Permeability measurements of modified class J and aluminous cement pastes cured hydrothermally were made using both pressurized (up to 13.4 MPa) water and pressurized (up to 0.55 MPa) nitrogen gas. Samples of the pastes were cured hydrothermally at 400°C and 34 to 69 MPa from 1 to 96 days. As shown in Figure D-1, the difference in permeability between samples cured within stainless steel rings and those later epoxy sealed into rings is negligible. If samples were not tested immediately after hydrothermal curing, the additional room temperature curing for these samples was also negligible; however, longer room temperature curing produced a lower permeability value.

The addition of high silica modifiers was also investigated. Perlite, a light weight SiO_2 modifier, produced samples with permeability values of 10^{-2} to 10^{-4} darcys whereas the calcined chrysotile additive produced samples with 10^{-7} to 10^{-9} darcys (Figure 11).

Figure D-1. Water Permeability for Hydrathermally Cured Modified Class J (J-1) Oil Well Cement Pastes

APPENDIX E

VISCOSITY

Comparisons in viscosity measurements for various modifications are discussed in the main text of this report. Figures E-1 to -5 are the actual data for the results discussed using the Brookfield rotational viscometer.

The calibration for this viscometer included using numerous standard calibration fluids. One such Newtonian fluid is shown in Fig. E-6.

More recent viscosity measurements were made with a Haake RV3 roto-visco viscometer using a serrated sensor SVIIP, which was designed especially for measurement of slurries such as cement pastes. Results from the viscosity measurements made at Dowell at 300°F are given below. Measurements on both 60/40 and 80/20 of class J cement/calced chrysotile mixtures were found to be pumpable at room temperature, up to 60°C (shown in Figure E-7).

<u>Viscosity Data</u>					
<u>Ex. Starting Material</u>	<u>Ratio</u>	<u>Retarder (D-28)</u>	<u>Water (tap)</u>	<u>Temp. (°F)</u>	<u>Set Time (Min.)</u>
16 480 g Class J oil well cement + 320 g calcined chrysotile	60/40	2 grams	385 ml	300	51
17 480 g Class J oil well cement + 320 g calcined chrysotile	60/40	6 grams	385 ml	300	381, still not set
18 640 g Class J oil well cement + 160 g calcined chrysotile	80/20	0 grams	385 ml	300	35
19 640 g Class J oil well cement + 160 g calcined chrysotile	80/20	2 grams	385 ml	300	101
20 640 Class J oil well cement + 160 g asbestos (chrysotile) fibers		No amount of admixture would reduce viscosity of these mixtures to a pumpable level.			
21 480 g Class J oil well cement 320 g asbestos (chrysotile) fibers

Figure E-1. Comparison Between Two Calcium Aluminate Cement Paste Viscosities with Lignosulfonate Added as a Retarder

CALCIUM ALUMINATE CEMENT + 5% PERLITE

CLASS J CEMENT WITH MODIFICATIONS SHOWN

Figure E-2. Viscosity Measurements on Calcium-Aluminate (a,b) and Class J Cement Paste (c,d) with Various Admixtures

Figure E-3. Rotational Viscometer Measurements

VISCOSITY
BROOKFIELD RHEOLOG
Spindle X (modified paddle)

Figure E-4. Viscosity Changes for Calcium Aluminate Cement Samples with no Admixtures but Varying Sizes of Quartz Grains

Brookfield Rheolog
Model 5X HBT
Spindle = X (modified paddle)

Figure E-5. Viscosity of MgO with a w/s Ratio of 1.5

Figure E-6. Viscosity Measurements on Paratone Calibration Oil

Figure E-7. Viscosity Measurements made on 60/40 and 80/20 Mixtures of Class J Oil Well Cement and Calcined Chrysotile, Using the Haake Rotovisco RV 3 and the Serrated SVIIP Sensor.

APPENDIX F

ELEMENTAL DISTRIBUTIONS

It was observed that, after curing in Tuscarora quartzite rock cylinders, C-M-S-H mixture 19 showed slight discoloration effects just inside the rock/cement interface. On one occasion, the central core of cement was removed from the rock cylinder and subjected to SEM examination to investigate the nature of the darkened ring. Figure F-1 and the accompanying schematic sketch depicts the results of a scan taken from the edge of the "dark" rim towards the cement core. The silicon content does not change from the "5-20-mm" values, whereas the calcium content increases as the beam is moved into the cement. This gradient suggests that there may be some interaction between the host rock and the cured cement. Thus, 5-mm represents high SiO_2 , low CaO ; maximal reaction of the quartzite with cement; the "10-mm" point an intermediate amount of reaction; while "15-20-mm" show that an equilibrium cement of constant composition has been reached.

To account for the color in the rim, there is possibly a slight migration of iron from the rock into the cement as is evidenced by the "5 mm" iron peak just inside the edge of the sample. The "mm" figures are measurements from the edge of the sample image displaced on the cathode ray tube at a 300X magnification; thus "1-mm" actually represents 3.3 μm .

Photographically reproduced SEM images of the mixture #19 and #20 cured for 36, 63, and 206 days are given in Figure F-2. Again, lath-like diopside is the predominant, stable run product after 206 days (6.75 months) of hydrothermal curing.

Figure F-1. Elemental Distribution for "Dark" Rim Between
Rock and Cured Class J Cement Paste

Figure F-2. SEM Photographs of Samples #19 and #20 Cured for 36, 63, and 206 Days at 400°C and 68.9 MPa (10,000 psi)

APPENDIX G

MANUFACTURER'S CEMENT SPECIFICATIONS

Typical chemical and physical properties of cement

	J-1	S-1	S-2	R-1
MgO		0.1	0.5	0.21
SiO ₂	34.6	0.2	0.30	4.2
Al ₂ O ₃	1.19	72	70.8*	59.3
Fe ₂ O ₃	1.20	0.1	0.25	1.8
CaO	36.6	26.0	27.2	33.5
SO ₃	0.25	nil		0.38
K ₂ O	nil	< 5%		nil
Na ₂ O				
sulfur sulfate	nil	nil		nil
loss on ignition	4.8			
200 mesh residue	17.1			
325 mesh residue	58.5			
specific surface (Wagner) cm ² /g	1575			
specific surface (Blaine) cm ² /gm			3800	
bulk density g/cm ³			0.96	
specific gravity			3.0	

*Includes TiO₂.

APPENDIX H
PUBLICATIONS

PAPERS PRESENTED

- E.L. White, C.A. Langton, M.W. Grutzeck, D.M. Roy. High-Temperature Cements for Geothermal Applications; Annual American Society Meeting, Refractories/Cements Joint Session, Cincinnati, May 1, 1979.
- D.M. Roy. High Temperature Cements for Geothermal Wells. SPE (AIME) Symposium on Geothermal and Oil Well Cements, Houston, Jan. 22-24, 1979.

PUBLISHED

- D.M. Roy, E.L. White, C.A. Langton and K.G. Zimmerman. Hydrated Calcium Aluminosilicate Cements Formed at Elevated Temperatures and Pressures. Cem. Concr. Res. 8, 509-512 (1978).
- D.M. Roy, E.L. White, C.A. Langton and M.W. Grutzeck. Potential New High Temperature Cements for Geothermal Wells. Proceedings, 1979 SPE Int'l. Symposium on Oilfield and Geothermal Chemistry, January 22-24 (1979). Houston: pp. 153-161.

IN PRESS

- D.M. Roy, C.A. Langton, M.W. Grutzeck and E.L. White. Hydrothermal High Temperature Cements for Potential Geothermal Applications, 1980 SPE international Symposium on Oilfield and Geothermal Chemistry, May 28-30, Paper No. 8994.
- C.A. Langton, E.L. White, M.W. Grutzeck and D.M. Roy. High Temperature Cements with Geothermal Applications, 7th International Congress Chem. Cement, Paris, 1980.

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- Brookhaven National Laboratory (1978b) Cementing of Geothermal Wells, Progress Report No. 9, Apr-June 1978.
- Brookhaven National Laboratory (1978c) Cementing of Geothermal Wells, Progress Report No. 10, July-Sept 1978.
- Brookhaven National Laboratory (1978d) Cementing of Geothermal Wells, Progress Report No. 11, Oct-Dec 1978.
- Brookhaven National Laboratory (1979) Cementing of Geothermal Wells, Progress Report No. 12, Jan-Mar 1978. BNL.