CEMENTING OF GEOTHERMAL WELLS

PROGRESS REPORT NO. 8 JANUARY - MARCH 1978

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Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Printed Copy \$9.00; Microfiche \$3.00

July 1978

500 copies

Abstract

A coordinated program for the development of improved cements specifically designed for geothermal well applications was started in April 1976. Since that time an assessment of the state of the art of well cementing has been made, a management plan prepared, and research on organic and inorganic cementing materials started. Work accomplished during the period January 1-March 31, 1978 is described in the current report.

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Research Institute

Summary

Work to implement the program plan for the development of improved high temperature cementing materials for geothermal wells is continuing. Research work is currently in progress at Brookhaven National Laboratory, Battelle's Columbus Laboratories, Colorado School of Mines, Dowell, Pennsylvania State University, Southwest Research Institute, University of Rhode Island, and the National Bureau of Standards.

Thermal gravimetric analysis studies on high temperature polymer cements have indicated that formulations containing organosiloxane are thermally stable at 350°C. Only slight (1%) weight losses at 400°C were measured. Samples exposed for 10 days to 25% brine at 238°C have not deteriorated. The relatively long curing time for some of the formulations (> 3 hr at 150°C) enhances the probability of being able to pump the materials.

Work to optimize PC systems containing cross-linked mixtures of styrene, acrylonitrile and acrylamide is continuing. Improvements in methods for curing the system have extended the thermal stability to the range 250°-300°C.

Differential scanning calorimeter and infra-red analysis studies are being performed on PC samples containing each of the chemical constituents of Type III portland cement and CaO compounds of anhydrous cements such as $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. The results indicate that $3\text{CaO} \cdot \text{SiO}_2$ derived from the chemical reaction between CaCO_3 and SiO_2 has a significant effect on the thermal stability of PC.

Work on the development of inorganic cementing materials is continuing at six laboratories. Several promising materials have been identified. Tests to measure compressive strengths, bond strengths, permeability, and compatibility with drilling muds are in progress. Consistometer tests have been performed on some materials.

Cementing of Geothermal Wells

Progress Report No. 8

January-March 1978

Introduction

The US Department of Energy, Division of Geothermal Energy, is sponsoring a research program to develop improved cementing materials for use in the completion of geothermal wells. The motivation for the program stems from an assessment that the cements currently used deteriorate in the geothermal environments, and that the life expectancy of a geothermal well and therefore the economics of geothermal power could be improved significantly if better materials are developed.

It is estimated that for use in geothermal wells, cementing materials with the following characteristics are needed:

1. Compressive strengths, > 1000 psi 24 hours after placement.
2. Permeability to water, < 0.1 milli Darcy.
3. Bond strength to steel casing, > 10 psi.
4. Stability, no significant reduction in strength or increase in permeability after prolong exposure at 400°C (~ 750°F) to 25% brine solutions, flashing brine, or dry steam.
5. Placement ability, capable of 3 to 4 hr retardation at expected placement temperatures.
6. Compatibility of the cement with drilling mud.
7. Non-corrosive to steel well casing.

The Process Sciences Division of the Department of Energy and Environment at BNL is assisting the Division of Geothermal Energy in

developing and managing a program that will result in the development of materials meeting the criteria listed above. The program represents an integrated approach to the definition, development, and implementation of the work. A successful development of improved materials will lead to a major advance in the technology required to economically utilize geothermal energy.

The goals for the overall program are as follows:

1. Preparation of an integrated research and development plan for the investigation of new well-cementing materials specifically designed for geothermal well applications.

2. To provide the technical basis for the development, testing, and practical demonstration of high-temperature cementing materials for geothermal wells.

3. Rapid transfer and implementation of the technology in the private sector.

The program goals will be achieved by performing the following tasks:

1. Develop well-cementing materials capable of withstanding the environmental conditions in geothermal wells.

2. Perform pilot-scale testing and analysis of the cementing materials at well down-hole conditions.

3. Develop the technology required to mix, pump, and place the cementing material.

4. Demonstrate the process by the cementing of a prototype well.

5. Perform cost analyses to determine the economic viability of the cementing systems under investigation.

6. Involve the well-cementing service industry and well owners in all phases of the program in order to provide a technical basis for the rapid implementation of the technology.

7. Prepare a comprehensive, high-temperature geothermal well-cementing manual which will include details of downhole equipment, pumps, cement properties, and field examples.

Planning work to organize and develop a management plan designed to meet the above objectives was started in April 1976. Experimental work was started in July 1976. The work at BNL involves in-house research on polymer concrete cementing materials as well as full management of an integrated program involving contract research and industrial participation.

This report constitutes the eighth in a series of quarterly reports describing work on the program. Accomplishments during the period January-March 1978 are summarized below. During the quarter work has continued in Tasks 1, 2, 3, and 7. Work was initiated in Task 4. Efforts in the other tasks will commence as the research work progresses.

Task 1. Program Management Plan

The need for DOE to sponsor a program to develop improved geothermal cementing materials was ascertained by evaluating information obtained from well owners, cementing service companies, and governmental and private research organizations. The consensus of those contacted was that the program should be a cooperative one performed on a cost-sharing basis with well cementing service companies and well owners. It was also established that the focal point of the program should be a series of down-hole test facilities. Testing should be performed in

several geothermal environments but the highest priority for near-term (~ 10 yr) application should be given to medium salinity brines at temperatures up to 400°C.

In an earlier report,¹ an outline of the approved management plan was presented. The program consists of the following elements: problem definition, materials development, property verification, down-hole testing, and the use of the cements in completing demonstration wells. The problem definition element has been completed and work is progressing in the materials development and property verification phases. Organizations currently participating in the program are as follows:

Problem definition, Dowell Division of Dow Chemical Co.

Materials development, Battelle's Columbus Laboratories

Brookhaven National Laboratory

Colorado School of Mines

Dowell Division of Dow Chemical Co.

Pennsylvania State University

Southwest Research Institute

University of Rhode Island

Property verification, National Bureau of Standards

As a means of obtaining technical guidance for the overall program and as an initial step in the technology transfer process, BNL has established a "Geothermal Well Cement Advisory Panel". The panel is affiliated as a Task Group of the American Petroleum Institute's (API) Committee on Standardization of Oil Well Cements. Mr. J. P. Gallus of Union Oil of California is Chairman of the Task Group. The next meeting of the panel is scheduled for June 20 and 21, 1978 at Dowell in Tulsa, Oklahoma.

Task 2. Selection of Well Cementing Materials

Work is being performed in this task to identify, evaluate, and select high temperature well cementing materials.

2.1 Polymer Cements

In the previous report,² work on the development of PC containing crosslinked mixtures of styrene (St), acrylonitrile (ACN), and acrylamide (Aa) was described. This work was continued during the current report period and studies on organosiloxanes were started. Both efforts are described below.

St-ACN-Aa Formulations

Results given previously² indicated that this monomer formulation crosslinked with trimethylolpropane trimethacrylate (TMPTMA) or divinyl benzene (DVB) produced PC with compressive strengths at 20°C up to 30,000 psi. The system also appears stable to hot brine and steam.

In the most practical sense, thermal stability is the ability of a material to maintain the required mechanical properties at a given temperature. One of the requirements for a thermally stable polymer is that it have a high melting or softening point. The use of many polymers is limited not by the breaking of chemical bonds but rather by changes in physical characteristics at elevated temperatures. They maintain their chemical structure but become weak, soft, and finally fluid.

The melting points of polymers may be increased by the introduction of polar substituents ($C \equiv N$) or by hydrogen bonding in groups such as amides. The presence of bulky substituents such as methyl groups increases the melting point by decreasing the mobility of the chain because it cannot fit together compactly.

The chemical factors affecting thermal stability are also very important. One is the formation of inter or intramolecular bonds on heating, resulting in crosslinked structures. Polymers may be cross-linked to structures which don't melt at all. Whereas the uses of thermoplastic materials are often limited by their softening point, thermoset materials are limited by the temperature at which bonds begin to break. Therefore, good heat resistant polymers must have bonds of high dissociation energy.

Unfortunately, predicting relative thermal stabilities of polymers involves more than comparing bond strengths. For example, ~ 78 kcal/mole is required to break the first bond in the chain of some vinyl polymers.

The products formed in this step are highly reactive free radicals. In the second step the chain further degrades to yield a monomer molecule and a shorter chain still bearing an odd electron.

The energy required to break the carbon-carbon bond in equation (1) is at least partially supplied through the formation of the double bond in the monomer unit which peeled off. Therefore, the thermal energy required to degrade vinyl polymers to monomers is less than the sum of the bond energies of the broken bonds.

Experiments are being performed to determine the thermal stability of St-ACN-Aa systems crosslinked with TMPTMA or DVB as a function of ACN and crosslinking agent concentration and the thermal treatment.

Results summarized in Table 1 show the weight loss of various monomer mixtures as a function of temperature and ACN concentration. All measurements were made using a DuPont 990 Thermogravimetric Analyzer (TGA). It can be seen from the table that at a temperature of 125°C, the concentration of ACN does not strongly affect the thermal properties of the copolymer. In the temperature range 200° to 300°C, increased ACN concentrations in the range 25 to 45 wt% result in increased stability if the concentrations of Aa and TMPTMA are invariable. Increasing the TMPTMA concentrations from 5 to 10 wt% while holding the ACN and Aa constant, results in increased thermal stability but decreased mechanical properties. The reason for this is that the introduction into the polymer chain of bulky substituents results in an increased melting point by decreasing the mobility of the chain. This reduces the mechanical properties.

In the temperature range 300° to 350°C, a rapid increase in weight loss of polymer occurs due to thermal oxidative degradation. As a result the mechanical properties of the polymer and the color are changed. The rate of thermal destruction of C-CN groups in the copolymer increases rapidly with temperature and results in the evolution of gases such as NH_3 , HCN, and H_2 .

The results from TGA studies on polymer samples, shown in Figure 1, indicate that in the temperature range 125° to 200°C the copolymers exhibit weight losses up to ~ 5%. Partial stabilization up to a temperature of ~ 300°C then occurs. In the range 300° to 350°C, complete degradation occurs.

Table 1
Weight Loss of St-ACN-Aa-TMPTMA Polymers
at Elevated Temperatures^a

Monomer composition, wt%				Polymer weight loss, %, at			
St	ACN	Aa	TMPTMA	125°C	200°C	250°C	300°C
65	25	7.5	2.5	0.6	3.68	5.0	5.65
60	30	7.5	2.5	0.4	3.68	5.0	5.45
50	40	7.5	2.5	0.4	2.55	3.75	4.4
45	45	7.5	2.5	0.4	2.50	3.75	4.95
62.5	25	7.5	5.0	0.6	5.00	7.5	8.6
57.5	30	7.5	5.0	0.6	3.70	5.4	6.25
47.5	40	7.5	5.0	0.6	3.70	5.0	5.6
42.5	45	7.5	5.0	0.3	2.53	4.3	5.4
60	25	7.5	7.5	0.6	3.75	6.25	7.5
55	30	7.5	7.5	0.4	2.7	5.0	6.25
45	40	7.5	7.5	0.4	3.1	5.0	6.1
40	45	7.5	7.5	0	1.8	3.1	4.15
57.5	25	7.5	10.0	0.1	3.5	6.2	7.4
52.5	30	7.5	10.0	0.1	2.6	5.5	6.85
42.5	40	7.5	10.0	0.3	2.5	4.3	5.25
37.5	45	7.5	10.0	0.3	2.1	3.65	4.35
67.5	25	2.5	5.0	0.3	3.5	5.1	6.2
62.5	30	2.5	5.0	0.3	2.4	3.9	5.0
52.5	40	2.5	5.0	0.4	2.4	3.75	4.0
47.5	45	2.5	5.0	0	1.25	2.3	2.5

a, measured in nitrogen using TGA

St, styrene

ACN, acrylonitrile

Aa, acrylamide

TMPTMA, trimethylolpropane trimethacrylate

Figure 1. Results from TGA studies on high temperature polymers.

Very recent data indicate that the weight loss exhibited at temperatures $< 250^{\circ}\text{C}$ may be due to unreacted monomer. One sample, finely ground, washed with ethyl alcohol to remove unreacted monomer, and then dried, had a weight loss of $\sim 5\%$. At 250°C the sample had a weight loss of 1% compared to 6.25% for an unwashed specimen. As a result of this observation, efforts are being made to develop improved methods for curing the formulations.

One method to enhance the degree of polymerization, therefore reducing unreacted monomer, is to increase the curing temperature. Results, shown in Table 2, indicate that large reductions in the weight loss at temperatures up to 300°C can be obtained by curing at different temperatures. As a result, improvements in mechanical properties occur. This is illustrated in Figure 2.

Work on this system is continuing.

Silicone PC

During the current report period work has been started to investigate PC materials containing silicones. A literature review indicated the following:

The term silicone is sometimes employed generically to all monomeric and polymeric organosilicone compounds containing Si-C bonds and sometimes as a collective term for organosilicon polymers of all types. However, it is also used in the more restricted sense of organosilicon polymers containing Si-O-Si bonds. Accordingly, we define silicones as organosilicon polymers in which the silicon atoms are bound to each other through oxygen atoms, the silicon valences not taken up by oxygen being saturated by at least one organic group. The prototype for the

Table 2

Weight Loss of St-ACN-Aa-TMPTMA Polymers at
Elevated Temperature as Effected by Curing Conditions
and Crosslinking Agent Concentration^a

Monomer composition, wt%				Curing method	Polymer weight loss, %, at			
St	ACN	Aa	TMPTMA		125°C	200°C	250°C	300°C
50	40	7.5	2.5	1	0.3	2.6	3.75	4.7
47.5	40	7.5	5.0	1	0.5	3.75	5.0	5.9
45	40	7.5	7.5	1	0.5	3.1	5.0	6.1
42.5	40	7.5	10.0	1	0.3	2.5	4.3	5.2
62.5	30	5.0	2.5	2	0	0	0	0.3
50	40	5.0	5.0	2	0	0	0	0.3
50	37.5	5.0	7.5	2	0	0	0.3	1.0
50	35	5.0	10.0	2	0	0.2	0.6	1.2

a, measured in nitrogen using TGA

St, styrene

ACN, acrylonitrile

Aa, acrylamide

TMPTMA, trimethylolpropane trimethacrylate

1, 60°C for 16 hr, 115°C for 3 hr

2, 60°C for 16 hr, 115°C for 3 hr, 160°C for 16 hr

Figure 2. Compressive strength as a function of curing temperature.

simple linear polymer is as follows:

The name siloxane was based on the formulation of the Si-O-Si unit as sil-oxane and this has found general acceptance in scientific nomenclature.

The composition of a siloxane unit is determined by the fact that each oxygen atom functions as a link between two silicon atoms so that each silicon atom can be considered to have only a half-share in each oxygen atom. The general formula of members of the above series is, therefore, $\text{R}_n\text{SiO}_{(4-n)/2}$.

The actual organosiloxane units are represented by this formula with "n" values from 1 to 3. The free valences on the oxygen determine the functionality of each siloxane unit. The organosiloxane units are therefore mono-, di-, or trifunctional. The nonfunctional molecule R_4Si cannot be used as a structural unit in polymers but the tetrafunctional structural group $(\text{SiO}_{4/2})$ is occasionally used with the others in the synthesis of organosiloxane polymers. The monofunctional siloxane unit can combine with itself only once, giving hexaorganodisiloxane $\text{R}_3\text{Si}-\text{O}-\text{SiR}_3$.

The difunctional units give closed rings on combination with one another giving 3, 4, or 5 siloxane units.

Trifunctional siloxane units combining with one another generally produce molecules cross-linked randomly in three dimensions.

A particularly interesting possibility is the combination of silanes or siloxanes with organic components by means of organofunctional groups to form relatively stable structures linked through Si-C bonds. There are some methods to polymerize and copolymerize an organosiloxane. One of them is with the organic group also involved in the reaction. The reaction proceeds through the unsaturated groups by heating the materials in air or with peroxide initiators. In this way a combination of silicon-carbon polymeric linkage is obtained. The degree of cross-linking through alefenic polymerization is much greater than if other polymerization methods are used.

Based upon this short review, work was started to determine applicability of using an organosiloxane to obtain high temperature mechanically and chemically stable PC. Preliminary results from this study are given in Tables 3 and 4. As can be seen in Table 3, the thermal stability of the copolymer based on the organosiloxane (OS) and styrene (St) is a function of the ratio of OS and St and dependent upon the content of the vinyl groups in the siloxane molecular chain. Table 4 summarizes preliminary

Table 3

Weight Loss of Siloxane Polymers at Elevated Temperatures^a

Monomer composition, wt%			Curing conditions ^b		Polymer weight loss, %, at			
OS	St	Crosslinking	time, hr	temp., °C	250°C	300°C	350°C	400°C
100	0	0	4	155	0.02	0.05	1.0	1.03
100	0	0	2	185	0.02	0.05	1.0	1.03
85	15	0	16	145	1.3	1.5	1.8	3.8
85	15	0	16	160	0.25	0.6	1.25	3.0
85	15	0	88	150	0	0	1.4	8.5
80	20	0	64	150	1.25	1.3	2.48	6.25
80	20	0	64	150	0.5	0.6	1.3	5.2
75	25	0	2	105	0	0	0	1.5
75	25	0	2.5	115	0	0	0	1.5
75	25	0	64	145	0	0	0	1.5
75	25	0	16	160	0.6	0.9	1.3	4.0
75	25	0	16	160	0.5	0.75	1.4	5.0
75	25	0	4	200	0.5	0.75	1.4	5.0
75	25	0	88	150	0.01	0.5	1.3	5.0
75	25	0	16	100	0	0	0.4	2.7
75	25	0	4	155	0	0	0.4	2.7
70	30	0	64	150	1.2	1.28	3.5	9.8
60	40	0	16	145	1.4	2.5	3.75	9.5
50	50	0	2	105	0.3	0.6	1.2	3.0
50	50	0	15	125	0.3	0.6	1.2	3.0
50	50	0	4	155	0.3	0.6	1.2	3.0
50	50	0	3	185	0.3	0.6	1.2	3.0
65	25	10 ^c	1	110	0.8	1.3	3.0	12.0
65	25	10 ^c	16	145	0.8	1.3	3.0	12.0
80	0	20 ^c	16	145	0.2	0.6	1.1	2.5
75	20	5 ^d	16	150	0	0	1.8	8.4
75	20	5 ^d	2.5	200	0	0	1.8	8.4
75	23.5	1.5 ^e	64	105	0.2	0.2	1.0	3.1
75	23.5	1.5 ^e	3	155	0.2	0.2	1.0	3.1
75	23	2 ^f	64	105	1.0	1.0	1.3	5.0
75	23	2 ^f	3	155	1.0	1.0	1.3	5.0
75	22	3 ^f	64	105	0.6	0.6	1.9	10.0
75	22	3 ^f	3	155	0.6	0.6	1.9	10.0

a, measured in nitrogen using TGA

b, 0.5 wt% di-t-butyl peroxide

OS, organosiloxane

St, styrene

c, TMPTMA

d, triallyl cyanurate

e, N-phenylmalimide

f, divinyl benzene

Table 4

Compressive Strength of Organosiloxane PC as a Function of Aggregate Size and Composition

Monomer composition, wt%		Aggregate composition, %	Compressive strength, psi
<u>OS</u>	<u>St</u>		
75	25	100% No. 500 sand	6034
75	25	65% No. 500 sand-35% Type III cement	2924
75	25	36% No. 16 sand-17% No. 30 sand-17% No. 100 sand-30% No. 50 sand	5849
100	0	same as above	1789
75	25	90% No. 500 sand-10% Type III cement	12,358
75	25	95% No. 500 sand-5% Fe ₂ O ₃	11,084
75	25	100% No. 30 sand	689
75	25	65% No. 30 sand-35% Type III cement	4588
75	25	100% No. 100 sand	370
75	25	65% No. 100 sand-35% Type III cement	3160

OS, organosiloxane
St, styrene

results of PC compressive strengths as a function of aggregate composition. The results indicate that the composition and particle size of the aggregate is very important in producing high quality PC. Thermal stability data at 260°C are plotted in Figure 3. Stability tests in brine at 238°C are currently being performed to determine if hydrolysis of the material will occur. Visual inspection after exposure for 10 days indicated no apparent deterioration. This work is continuing.

Aggregate Research

During the testing of PC samples in steam at 238°C, it was observed that samples containing portland cement which was added to the aggregate as a fine filler exhibited better durability than specimens not containing cement. As a result, a study to determine the cause of this effect is in progress.

In the initial phase of this work, the major chemical constituents of Type III portland cement (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO and MgO) were combined with silica sand and vinyl-type monomers such as methyl methacrylate (MMA) and St to form PC. The results from thermal stability tests shown in Figure 4 and from compressive strength measurements indicate that CaO , the major constituent of portland cement, had the greatest effect on stability after exposure to hot air.

The effect of CaO on stability in hot brine could not be determined due to large dimensional changes caused by the chemical reaction between CaO and water (see Figure 5). As a result, studies are performed using CaO compounds of anhydrous cement such as tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$) dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) and tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$).

Figure 3. Thermal stability at 260°C of PC containing organosiloxane.

Figure 4. Effect of Type III portland cement and chemical constituents of cement on weight loss of PC after exposure for 30 days to hot air at 238°C.

Figure 5. Changes in weight and diameter of PC containing Type III portland cement and chemical constituents of cement after exposure for 30 days to 25% brine at 238°C.

Currently Differential Scanning Calorimeter (DSC) and infra-red analysis (IR) studies are being performed on PC samples containing each of the above compounds in conjunction with polymethyl methacrylate (PMMA). The results from the DSC thermograms indicated that $3\text{CaO}\cdot\text{SiO}_2$ derived from the chemical reaction between CaCO_3 and SiO_2 had a significant effect on the thermal stability of PMMA.

The thermograms of PMMA containing $3\text{CaO}\cdot\text{SiO}_2$ (Figure 6) did not exhibit a noticeable endothermic peak in the range $160^\circ\text{--}200^\circ\text{C}$ compared with that of $\text{PMMA-CaCO}_3\text{-SiO}_2$ systems (Figure 7). Generally, the first endothermic peak of PMMA itself is characterized by the double peaks at 180°C and 193°C . The first broad peak actually represents the change from the crystalline solid to a liquid crystal state. The thermal decomposition of PMMA, therefore, is considered to occur in the temperature range of $150^\circ\text{--}210^\circ\text{C}$.

The endothermic peak near 200°C of PMMA samples combined with CaO-SiO_2 systems has a tendency to disappear with increasing CaO contents (see Figure 6). If the onset temperature of endothermal effect is not considered, the thermograms of $\text{PMMA-}3\text{CaO}\cdot\text{SiO}_2$ systems indicate that the first endothermic peak for PMMA is increased from $\sim 180^\circ\text{C}$ to $\sim 303^\circ\text{C}$ due to the addition of 66 wt% $3\text{CaO}\cdot\text{SiO}_2$.

As an attempt to better understand the effect of CaO in CaO-SiO_2 systems on the thermal stability of vinyl-type polymers, the heat of fusion of the first peak in the region of $180^\circ\text{--}210^\circ\text{C}$ for these samples was calculated.

The heats of fusion of PMMA and PMMA samples containing $\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot 2\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$, and type III portland

Figure 6. Differential scanning calorimeter thermograms of PMMA - CaO - SiO₂ Systems. a, bulk PMMA; b, 34 wt% PMMA-66 wt% CaO·SiO₂; c, 34 wt% PMMA - 66 wt% 3CaO·2SiO₂; d, 34 wt% PMMA - 66 wt% 2CaO·SiO₂; e, 34 wt% PMMA - 66 wt% 3CaO·SiO₂.

Figure 7. Differential Scanning calorimeter thermograms of PMMA samples. a, 34 wt% PMMA - 66 wt% CaCO_3 ; b, 50 wt% PMMA - 50 wt% SiO_2 ; c, 34 wt% PMMA - 66 wt% cement; d, 34 wt% PMMA - 66 wt% $3\text{CaO} \cdot \text{SiO}_2$.

cement, were 34.93 cal/g, 4.99 cal/g, 3.07 cal/g, 1.74 cal/g, 0.00 cal/g, and 1.23 cal/g, respectively. The heat of fusion of PMMA containing 66 wt% type III portland cement was 1.23 cal/g. These data indicate that the $3\text{CaO}\cdot\text{SiO}_2$ component of cement has the greatest effect on thermal stability of vinyl-type polymers.

From IR spectras (Figure 8) it has been noted that the absorption band of the $-\text{CH}_2$ -group for the region $3000\text{--}2900\text{ cm}^{-1}$ of PMMA becomes smaller with increased CaO content in $\text{CaO}\text{--}\text{SiO}_2$ systems. Also, the IR spectras of PMMA containing $3\text{CaO}\cdot\text{SiO}_2$ and type III portland cement were observed to have very similar absorption bands which contained smaller bands at 3020 cm^{-1} and 2970 cm^{-1} than those of PMMA.

To obtain further information about the interaction between the $3\text{CaO}\cdot\text{SiO}_2$ and the $-\text{CH}_2$ -group, a quantitative analysis was performed by using the IR absorbance ratio obtained by dividing the absorbance of the $-\text{CH}_2$ -group at 2970 cm^{-1} by the absorbance of the $-\text{C}=\text{O}$ group at 1730 cm^{-1} . These results indicate that the absorbance ratio of PMMA containing $3\text{CaO}\cdot\text{SiO}_2$ is almost the same (0.23 vs 0.25) as that of PMMA containing type III portland cement.

Based upon the data obtained to date, a chemical interaction between CaO and the $-\text{CH}_2$ groups in the vinyl monomers may occur.

The work is being continued with a mechanical evaluation, DSC study and IR analyses after exposure of samples for 30 days to 25% brine at 238°C .

Inorganic Cements

Research on high temperature inorganic cements is in progress at six laboratories. The status of each program is summarized below.

Figure 8. Infrared spectra of PMMA-CaO-SiO₂ systems before exposure to hot brine.

Colorado School of Mines

G. L. Kalousek, Principal Investigator

Starting date, April 1977

Status: The third and fourth quarterly reports for the program are given in Appendix 1 and 2.

University of Rhode Island

T. J. Rockett, Principal Investigator

Starting date, July 1977

Status: The third quarterly report for the program is given in Appendix 3.

Dowell Division of Dow Chemical

B. E. Simpson, Principal Investigator

Starting date, July 1977

Status: A Phase I report summarizing the state of the art of well cementing was given in the previous report.² The second quarterly report for the program is given in Appendix 4.

Battelle's Columbus Laboratories

R. S. Kalyoncu, Principal Investigator

Starting date, September 1977

Status: The second quarterly report for the program is given in Appendix 5.

Pennsylvania State University

D. M. Roy, Principal Investigator

Starting date, September 1977

Status: The second quarterly report for the program is given in Appendix 6.

Southwest Research Institute

D. K. Curtice, Principle Investigator

Starting date, October 1977

Status: The second quarterly report is given in Appendix 7.

Task 3. Mechanical, Physical, and Chemical Resistance Property Measurements

In conjunction with work performed in Task 2, tests to measure the mechanical, physical and chemical resistance properties of high temperature cementing materials are being conducted.

Samples of polymer cement containing 50 wt% St-33 wt% ACN-17 wt% TMPTMA and 55 wt% St-36 wt% ACN-9 wt% TMPTMA were removed from a well-head test chamber at The Geysers after exposure to dry steam at 238°C for 2 years. These samples, shown in Figure 9, had compressive strengths ranging between 2278 psi (sample X-10) and 335 psi (X-8). The average strength and water absorption was 1570 psi and 8.5%, respectively. Earlier samples evaluated after exposure for 180 days had values of 2350 psi and 8.7%.

Test series No. 3, consisting of 48 cylinders, was placed into test in November 1977. Four monomer systems: 80 wt% St-12 wt% polyphenylene oxide-8 wt% TMPTMA, 30 wt% St-60 wt% triallyl cyanurate-10 wt% polyphenylene oxide, 55 wt% St-35 wt% ACN-5 wt% Aa-5 wt% TMPTMA, and 50 wt% St-40 wt% ACN-5 wt% MAa-5 wt% TMPTMA in conjunction with sand-cement aggregate are being evaluated. Results are not yet available, but based upon earlier work, these systems are expected to yield improvements over the results obtained in Series No. 1 and 2.

Testing of inorganic cements has been started at each of the six laboratories participating in that portion of the program. Results are given in Appendicies 1-5.

A testing program that will be precursor to down-hole evaluation is in progress at the National Bureau of Standards. Test procedures have been developed and equipment assembled. Samples of oil well cements

Figure 9. PC specimens after exposure for 2 years to dry steam at 238°C.

used for the completion of geothermal wells are in test. A progress report for this program has not yet been received.

Task 4. Placement Technology

Work has been initiated in this task during the current report period. To date, thickening time tests have been started on cements identified at Dowell, Battelle's Columbus Laboratories and Southwest Research Institute. The latter two studies are discussed in Appendices 3 and 5, respectively.

Task 7. Administrative

During the current report period, three "Monthly Administrative Letters" were submitted to DGE and Quarterly Progress Report No. 7² was issued.

References

1. Cementing of Geothermal Wells, Progress Report No. 2, July-September 1976, BNL 50578.
2. Cementing of Geothermal Wells, Progress Report No. 7, October-December 1977, BNL 50808.

Distribution

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Appendix 1

Third Quarterly Technical Report

October 1, 1977 to December 31, 1977

BNL/DOE Contract No. 406003-5

"DEVELOPMENT OF CEMENT FOR USE

IN GEOTHERMAL AND DEEP OIL WELLS"

Introduction

The more significant findings particularly during this quarter are summarized in this report. The following tests are being conducted: Compressive strength, volume change in water and a saline solution, compressive strength after exposure to the saline solution, bond strength between cement and formation (wallrock) and between cement and steel, compressive strength of formation fines and cements as a supplement to the cement-formation bond strength, and effects of perlite, fly ash and bentonite added to the cements. X-ray diffraction is used for phase identification for explaining properties of the cements. Tests on permeability of the cements, corrosion of the steel and consistency of the slurries are postponed until two or three candidate cements are established on the basis of the other tests.

The specimens are cured at 150 to 350°C and saturated steam pressure. Facilities for autoclaving up to 400°C and 20,000 psi pressure are being modified by the vendor to stop leakage through the seal. Autoclaving cycles of 1d at 150°C (precure), 20d at 250°C and 7d at 300°C were used in some of the strength tests. Currently the curing cycles after the 150°C precure are 7d at 175°C, 7d at 250°C and 7d at 350°C.

Some of these cycles for certain compositions were ample and others were probably inadequate for attaining equilibrium. The 7-day cycle was an expediency to accelerate production of data. Later tests on a select and limited number of candidate cements will be conducted on specimens demonstrated to have reached equilibrium at each selected temperature. The practice of increasing the temperature to accelerate the reaction is valid only when the same phase or phases are formed at the higher temperature as at the lower temperature. An important example of this procedure is the breakdown of tobermorite into xonotlite and gyrolite at about 150 to 220°C with accompanying increase in porosity or permeability and reduced strength. Tobermorite in long-time curing is stable up to about 150°C. In cements such as those of this study, tobermorite may be formed as the only binder in 24 hours at 175 to 200°C but continued curing at these temperatures results in the cited breakdown.

Phases That Form in Calcium Silicate Cements

Calcium silicate cements with silica and extraneous constituents form the following phases depending on compositions and autoclave cycles.

<u>Name</u>	<u>Formula</u>	<u>Property of Pure Phase</u>
CSH (1) ^a	(gel-like) indefinite	Very high strength
Tobermorite	$C_5S_6H_5$	High strength
Xonotlite	C_6S_6H	Moderate strength - porous
Truscotite	$C_7S_{12}H_2$	Possible moderate to low strength
Gyrolite	$C_2S_3H_2$	Low strength
"3.15 A phase"	$C_5S_6H_x$	Unknown

(a) In the formulas C=CaO, S=SiO₂, H=H₂O, $\bar{C}$ =CO₂, N=Na₂O, A=Al₂O₃ and F=Fe₂O₃

<u>Name</u>	<u>Formula</u>	<u>Property of Pure Phase</u>
Scawtite	$C_7S_6\bar{C}H_2$	Unknown
Pectolite	NC_4S_6H	Possible moderate strength
Alpha dicalcium silicate hyd	αC_2SH	Very weak and porous
Hydrogarnets	$C_3(A_{1-x}F_x)(H_{6-y}S_{2y})$	Very weak

Materials and Procedures of Test

The principal starting materials are a Class G and a Class J cements and a silica developed for oil well cements. Fly ash, perlite and bentonite clay of approved quality for oil well cements are supplemental materials as additives to the cement. Alumina is added as reagent grade gibbsite, $Al_2O_3 \cdot 3H_2O$. In limited number of tests Fe_2O_3 is added as goethite, and Na_2O as NaOH. The CO_2 leading to formation of scawtite is present in small amounts in the Class J. cement.

The compositions of the Class J and Class G cements were modified by additions of the silica to give CaO/SiO_2 molar ratios (C/S) of 0.6 to 0.8. In some tests the C/S ratio of the Class J cement was increased to 1.0 C/S by addition of reagent quality $Ca(OH)_2$. The Class J cement consisting of relatively pure βC_2S and silica was amenable to adjustment to exact compositions with and without Al_2O_3 of $0.6 CaO/SiO_2 + Al_2O_3$ ^(a) to 1.0 C/S. The Class G cement made of a portland cement and containing Al_2O_3 , SO_3 , MgO , etc. could not be adjusted to exact compositions because of the uncertainty regarding the disposal of the extraneous components in reaction products except Al_2O_3 into tobermorite and xonotlite. In the computations of compositions of the Class G cements, the Al_2O_3 was

(a) The ratio is expressed as $C/(S+5A)$ for 5% Al_2O_3 and other Al_2O_3 additives

counted as SiO_2 and the other components were disregarded. The compositions are reported as 0.6, 0.8 and 1.0 C/S. The amount of Al_2O_3 computed as replacement for SiO_2 , on an Al^{3+} for Si^{4+} , were reported on weight basis of Al_2O_3 by weight of CaO plus SiO_2 plus Al_2O_3 . In the limited number of tests involving Fe_2O_3 and Na_2O , both were computed as percent by weight of the cements on an anhydrous basis.

The saline solution consisted of 0.2 moles of Na_2CO_3 and 0.2 moles Na_2SO_4 per liter of solution, or 4.8% of the salts on anhydrous basis.

The additions of water to the cement were such as to yield a slurry which was relatively fluid for easy placement in the mold, but not so high as to cause subsidence of the solids. The apparently optimum water/solids ratio of the G Class cement was 0.38 and that of the Class J cement, 0.45. The additions for modifying the mix compositions also modified the water requirements.

Compressive strengths were obtained on 1-inch cubes precured in the molds in an autoclave for 24 hours at 150°C followed by other cycles of autoclaving. The precuring was necessary with the Class J cements because these harden very slowly at ordinary temperatures. For purposes of direct comparison, the Class G cements were similarly precured. The Class G cements, however, are also being cured in a moist cabinet at 73°F for 24 hours and then subjected to the other curing cycles.

The volume change specimens, 1x1x5 inch in size, were processed the same as the cubes. They were provided with standard reference points in the ends of the bars and measured with a standard comparator. Prior to the initial and other length measurements, the bars were stabilized to constant length in 73°F water.

Two procedures are being followed in determining the formation (rock) - cement bonds. A "push out" test was adapted for a direct measure of the bond and also of the steel-cement bond. The specimen, 3/4 inch in diameter by 2 inches, is carefully centered and firmly held in position in a 1-inch deep by 2 inch diameter mold. The cement is puddled around the specimen to a depth of 1 inch and covered with plate containing a 3/4 inch dia. opening in the center. The assembly is precured at either 150°C or 73°F, as required in the test. The specimens are then autoclaved at selected time-temperature cycles. The processed specimens are placed in a compression machine on a base plate provided with a snug-fitting opening into which the bar is pushed. The rack or steel specimen is loaded to the point of yield and then further loaded to cause extrusion of the entire specimen. Both loads, as measure of the bond strength, are recorded.

The rocks selected for these and any other tests were considered to be representative of the formation rocks: granite, shale, basalt, rhyolite, calcite, dolomite, sandstone and siltstone (from the Imperial Valley formation). Other possibilities are serpentine, graywache and chert encountered in the Geysers area.

Compressive strengths of cubes made of 50% (-20 + 100 mesh sieve) formation fines and 50% of a Class J and Class G cements are a basis for determining formation-cement compatibility at elevated temperatures.

The rock specimens cored from a piece of rock are not polished to eliminate surface irregularities. The bond strength, therefore, consists of a combination of mechanical and chemical bond of cement and formation or steel.

Because of the complex nature of the bonds, it appeared desirable to determine the compressive strengths of the cement-fines compositions as a supplemental measure of bonding of cement and rock.

Compressive Strength

It had been reported that 7% Al_2O_3 substitution in tobermorite at 0.83 C/S composition increased the temperature stability to 250°C in saturated steam and increased strength by 50 to 100%. Compositions of 0.63 and 0.70 C/S indicated similar improvements. The results on the 0.6 C/S composition at high temperatures were questionable.

The present tests were conducted on similar compositions as the earlier tests. Curing at 250°C for 20 days confirmed the earlier results but at higher strengths. Aluminous tobermorite was the phase at both ages of curing and, therefore, it is considered that equilibrium had been attained between 7 and 20 days for these compositions. The mixes consisted of Class J Cement with additions of silica and alumina. The results for the 0.7 C/(S+A) products with 0.0 to 7.5% Al_2O_3 are given in Figure 1. Curing at 150°C for one day was included to indicate effects of Al_2O_3 on early strengths. Curing at 250°C for 20 days caused increasing strength with increasing Al_2O_3 content which at 5% Al_2O_3 was about 10,000 psi. At 300°C for 7d, the 0.0 and 2.5% Al_2O_3 content yielded higher strengths than at 250°C , but the higher Al_2O_3 contents showed a marked strength decrease. It follows that the aluminous tobermorite stable at 250°C was not stable at 300°C indicating decomposition of the tobermorite. At 150°C curing for 1d to indicate effect of Al_2O_3 on early strength, the 2.5% addition had no effect but at 5.0% Al_2O_3 the strength had dropped to 1000 psi and to 250 psi at 7.5% Al_2O_3 . The highly beneficial effects

of Al_2O_3 would appear to be restricted to amounts of 2.5 to 5.0%.

The 0.63 C/(S+A) gave results nearly identical to those of the 0.70 C/(S+A) compositions, and for the 0.60 C/(S+A) the trends were highly similar but the strengths generally were lower. At 250°C the binder was aluminous tobermorite and residual quartz. The results for the 0.83 C/(S+A) were similar to those at 0.7 C/(S+A) , but generally the strengths were lower. This was attributed to increased W/S necessitated by additions of $\text{Ca}(\text{OH})_2$ and the Al_2O_3 in form of kaolin in this particular series.

On the basis of these results, it is considered that up to 5% Al_2O_3 substitution in tobermorite would be a possible modification of tobermorite to increase its stability to 250°C and its strength in the range of 10,000 psi.

Additions of 2% of Na_2O as NaOH to all the above compositions had the effect of decreasing the strength of the 1 day - 150°C specimens. The strengths at 250 and 300°C for all compositions were also decreased to the range of 3500 to 5000 $^\circ\text{C}$, with only small effects of Al_2O_3 being manifested. The Na_2O was added as NaOH to avoid introduction of an extraneous ion and was intended to provide some information on effects of Na_2O at later ages.

The Class G cements in compositions of 0.6, 0.8 and 1.0 C/S were tested similarly as the Class J cements. These cements, at W/S of 0.38, and cured at 250 to 350°C gave high strengths, 7500 to 11,500 psi. Direct comparisons of the Class G and Class J cements cannot be made. The Class G cements developed an entirely different kind of binders compared to those of the Class J cements. The results on binders are discussed in connection with volume changes in the next section of this paper.

Volume Changes of Cements During Water Storage at 150 to 350°C

The length changes of the bars of Class J cement at 0.6 C/S, 0.6 C/(S+5A), 0.85 C/S, 0.83 C/(S+7A) and 1.0 C/S, and of the Class G cements at 0.6, 0.8 and 1.0 C/S at 175⁰ to 350⁰ - 7 day exposure are reported in Figure 2. The phases found in small companion specimens processed simultaneously with the 1x1x5 inch bars are listed in Table 1.

All the Class J cements cured for 1 day at 150⁰C contained a poorly crystallized tobermorite and various amounts of reactants depending on composition. Quartz predominated in amount in the 0.6 C/S compositions, and decreased in amount with increasing C/S ratio. Class G cements at all C/S ratios and cured for 1 day at 150⁰C contained only α -C₂SH, CSH(1) and surprisingly only trace amounts of the cement; quartz was detected in all the samples.

The 0.6 C/S Class J cement cured at 175⁰C contained tobermorite, scawtite and residual quartz; at 250⁰C the tobermorite had transformed to gyrolite and to truscotitte at 350⁰C. The volume increase appears to be associated with formation of gyrolite (unless other undetected alteration occurred). Addition of Al₂O₃ to the 0.6 C/S composition prevented scawtite formation, and the only detected binder at 175⁰ and 250⁰C was tobermorite which transformed to truscotitte at 350⁰C. The tobermorite to truscotitte transformation is associated with a relatively large shrinkage, 0.12%. The 0.85 C/S contained some scawtite at all three temperatures; the tobermorite at 175⁰C transformed to gyrolite at 250⁰C with a small expansion; at 350⁰C the gyrolite transformed to truscotitte with a relatively large shrinkage, 0.11%. The addition of Al₂O₃ to this cement also prevented formation of scawtite; the only detected binder

at 175 and 250°C was tobermorite which in this temperature interval underwent shrinkage. Between 175 and 350°C, the tobermorite transformed only partially to truscotite, and tobermorite was still present at 350°C. The diffractometer indicated a change in the d spacing values, but due to the limited sensitivity of this instrument, a conclusion to this effect is not made. It is planned to study this phase with the Guinier Camera and analysis of single crystals. The shrinkage between 175 and 350°C of 0.24% appears too large not to have adverse effects. At 1.0 C/S and between 175 to 350°C, the volume change was very small, and the detected binder was predominately xonotlite along with a little scawtite.

The Class G cements showed entirely different binders from those observed for the Class J cements. The CSH(1) detected at 150°C transformed to tobermorite at 175°C at 0.6 and 0.8 C/S and to xonotlite at 1.0 C/S; the α C₂SH persisted. The phase change between 150° and 175°C was accompanied by a small volume increase. At 250°C, all the α C₂SH and tobermorite had apparently reacted with silica to form xonotlite with a moderate increase in volume. The xonotlite in the 0.6 and 0.8 persisted as such at 350°C along with formation of an unidentified phase indicated by a strong spacing at 11.3A in the 0.8 C/S product. The shrinkage of the 0.8 C/S product between 250 and 350°C was relatively large, 0.15%. The 1.0 C/S composition between 250 and 350°C, on the other hand, underwent an expansion; the diffractometer showed xonotlite at both temperatures. The phase changes of the Class G cements detectable by the diffractometer were inadequate to explain the volume changes of specimens in which xonotlite was the dominant phase.

Linear Change of Bars in Saline Solution

Bars of the same compositions as in the elevated temperature water exposure tests were stored in a saline solution ($0.2\text{MNa}_2\text{SO}_4$ plus $0.2\text{MNa}_2\text{CO}_3$). The bars previously exposed in water through 350°C were also placed in the same saline solution. The previous procedures of determining length changes were followed in these tests. (The 1.0C/S Class J cement bars for the saline water exposure were accidentally broken).

The results in Figure 3 show that expansions of all Class J cements were of small to moderate extent, 0.04 to 0.09%, at 175°C . At 250°C , the compositions without Al_2O_3 showed larger expansions than those with Al_2O_3 . Marked increase in expansion occurred at 350°C for most compositions particularly those without Al_2O_3 , these being 0.30, 0.23 and 0.09% for the 0.6, 0.85 and 1.0 C/S bars, respectively. The bars previously cured in water through 350°C exhibited the same trend for results as the others at 350°C .

The Class G cements at all compositions underwent small to moderate expansions, 0.02 to 0.07%, over the 175 to 350°C range.

The difference in results between the two classes of cements is not reconcilable on the basis of C/S composition. Either the extraneous constituents or the differences in the hydration products and their transformations in the Class G cements affected the extents of volume changes. (The identification of the binders will be made later in the program).

Effect of Saline Solution on Strength

The same compositions as above were used in further strength tests, and the results are given in Figure 4. The overall strengths of the Class G cements ranged from about 4,000 to 8,000 ps except that for

the 1.0 C/S mix cured at 250°C which was 2,600 psi. The volume changes in the saline solution at 175 and 250°C do not correlate with strength. At 350°C the two Al_2O_3 -containing mixes had the largest strength losses, although it was the Al_2O_3 - free mixes which underwent the largest expansion. The xonotlite composition (1.0 C/S) showed progressive strength losses going from 175°C to 350°C. Phase identification of these binders might reveal the cause of this loss and will be made later.

The trends of strengths for the Class G cements were distinctly different from those of the Class J cements. At 175°C, the strength decreased significantly, going from the 0.6 to the 1.0 C/S compositions. The reverse occurred at 250 and 350°C, the strengths showing marked increases.

It is realized that the 7-day curing may be inadequate for completion of the saline solution attack on the cements. The results, however, indicate trends which will be helpful in designing further tests.

Effects of Curing at 350°C on Strength

As mentioned earlier in this report, the 0.6 C/(S+A) compositions cured at about 300 - 325°C exhibited a tendency to weak strength with the binder being truscottite or truscottite-gyrolite intergrowths. The 0.6 C/(S+A) compositions cured at 250°C, on the other hand, were high strength binders. The present tests were concerned with progress of strength between 7 and 90 days at 350°C for 0.6 C/S and 0.6 C/(S+5A) compositions of Class J cement at W/S of 0.41 and 0.6 C/S and 0.8 C/S compositions of Class G cement at W/S of 0.37. The 0.8 C/S mixes were included for the Class G cement because of its otherwise difference in behavior from the Class J cement. The results in Table 2 show the

strengths of the 0.6 and 0.6 C/(S+A) are similar, and the variations due to time of autoclaving are in the order of reproducibility of the results. It is, therefore, tentatively considered that time of curing at 350°C after about 7 days has little if any effect on strength. The effects of admixtures and other W/S ratios remain to be determined; also, a complete phase identification of these and other related phases is planned. The 0.6 C/S at 7 days consisted of truscotite as dominant phase and a little scawtite along with a little quartz. The 0.6 C/(S+5A) binder consisted of truscotite and little quartz.

The 0.6 C/S Class G cement also showed relatedly small strength differences at 7, 30 and 90 days, the strengths were high. The binders in preliminary diffractometer examination were predominantly xonotlite and quartz at the three temperatures with minor amount of truscottite. The cell parameters of Xonotlite showed Al^{3+} substitution.

The 0.8 C/S Class G cement gave very high strength at 7 days, and the binder was essentially xonotlite and quartz. The strength retrogressed at 30 and 90 days, but remained high. (These specimens are planned to be carefully studied for phase content).

Table 2 Effect of Curing at 350°C For 7 to 90 Days

Time - Days	Class J		Class G	
	0.6 C/S	0.6 C/S+A	0.6 C/S	0.8 C/S
7	3,000	3,450	6,800	12,200
30	3,400	3,350	7,000	10,200
90	3,150	3,100	6,600	8,300

Bond Strength Tests

The search continues for ample-size rock specimens for measuring the rock-cement bond in shear and as compressive strengths. Two rocks, granite and basalt, are on order to provide in excess of 100 3/4 inch D by 2 inch cylinders. Three rocks, shale, granite and sandstone, available at the School in small lots, have been cored and the residues as -20, +100 mesh sieve fines used in compressive strengths. The Bureau of Reclamation supplied limited amounts of shale and sandstone also available at the School, and limestone, serpentine and siltstone.

Currently the cement-steel composites are being fabricated and processed for test.

Initial results on the compressive strengths indicated a difference in strength between a Class J cement at 0.83 C/(S+7A) and Class G cement at 1.0 C/S with the rock fines, one difference being significant; additional tests are now in progress and results will be submitted when these are completed.

Discussions

No conclusions are being drawn on results to date; the tests have been on cements without admixtures and at different W/S ratios. A program on effects of perlite, fly ash and bentonite and different W/S ratios has been initiated. The precuring of the Class G cements at 150°C for 1 day yielded unexpected hydration products, and the effects of other temperatures of precuring on this cement are underway.

The results on the Class G cements given in this report appear excellent for the properties tested. The next series of tests mentioned

above and others will disclose more fully the properties of the two classes of cement. The persistence of xonotlite as a strong binder in the 0.6, 0.8 and 1.0 C/S at 350°C in the G class cements is raising some interesting points. The extraneous constituents, Al_2O_3 , Fe_2O_3 , MgO , SO_3 , etc. may be factors in this cement.

The volume change measurements show up to sizeable expansions for certain compositions and autoclave cycles, and sizeable shrinkages for others. Tentatively, it may be speculated that some of the cements under certain conditions possess "built-in" expansive capabilities. The benefit of small expansions of well cements is well recognized. Exposure of the cements in the saline solution at 175 to 350°C caused expansions of the 0.6 to 0.85 C/S Class G cements; these at 350°C were about 0.3 and 0.2% respectively. The compressive stress developed in the cements at these higher expansions could cause failure of weaker porous formations.

Shrinkage of any significant extent of the cement is questionable. It may cause weakening or rupture of the formation-cement and/or steel-cement bonds or even cracks through the cement annulus between formation and steel.

The shrinkages of the Class J cements at 0.6 and 0.85 C/S were related at least in part to the formation of truscottite. The large shrinkage of the 7% Al_2O_3 substituted tobermorite may be due at least in part to a change in cell size of the tobermorite at 350°C as suggested (but not proven) by the diffractometer.

It is not yet apparent if formation of scawtite instead of xonotlite in the Class J cement had any effects, good or bad, on properties. The Class G cements contained insufficient CO_2 to form scawtite.

Summary

Present research on the Class J cements confirmed that Al^{3+} substitution in tobermorite increased temperature stability to $250^{\circ}C$ and also significantly increased strength. The volume stability of the products with and without Al_2O_3 related at least in part to phase transformations: tobermorite $\rightarrow$ gyrolite caused expansion, and gyrolite $\rightarrow$ truscottite caused shrinkage. Also, the large shrinkage of a 7% Al_2O_3 tobermorite at $350^{\circ}C$ appeared to be due partly to a modification of the tobermorite. The Class G cements generally gave higher strengths and smaller volume changes than the Class J cements. The binder in the 0.6 and 0.8 C/S products at 250 and $350^{\circ}C$ was predominantly xonotlite, a little truscottite and residual quartz. The persistence of xonotlite as a metastable phase may indicate a very slow rate of transformation to truscottite.

Table 1 Phases Formed in Class J and Class G
Cements in 7 Days at 175, 250 and 350°C

Cement J			Cement G		
Composition	Temp. °C	Phases ^(a)	Composition	Temp. °C	Phases ^(a)
0.6 C/S	175	Tob., Scaw.	0.6 C/S	175	$\alpha\text{C}_2\text{SH}$, CsH(1)
	250	Gyr., Scaw.		250	Xon., Trus. ^(b)
	350	Trus., Scaw.		350	Xon., Trus.
0.6 C/(S+5A)	175	Tob.	0.8 C/S	175	$\alpha\text{C}_2\text{SH}$, CSH(1)
	250	Tob.		250	Xon., Trus.
	350	Trus.		350	Xon., Trus.
0.85 C/S	175	Tob., Scaw.	1.0 C/S	175	$\alpha\text{C}_2\text{SH}$, Xon.
	250	Gyr., Scaw.		250	Xon.
	350	Trus., Scaw.		350	Xon.
0.83 C/(S+7A)	175	Tob.			
	250	Tob.			
	350	"Tob.", Trus.			
1.0 C/S	175	Xon., Scaw.			
	250	Xon., Scaw.			
	350	Xon., Scaw.			

(a) Residual amounts of quartz or $\beta\text{C}_2\text{S}$ are not shown.

(b) Amounts of truscottite were very small to small.

Figure 1. Compressive strengths in water

Figure 2. Linear changes of cements in water

Figure 3. Linear changes of cements in saline water

Figure 4. Compressive strength in saline solution

Appendix 2

Fourth Quarterly Technical Report

January 1, 1978 to March 31, 1978

BNL/DOE Contract No. 406003-5

DEVELOPMENT OF CEMENT FOR USE IN GEOTHERMAL AND DEEP OIL WELLS

Introduction

This report covers continuation of the research described in the Third Quarterly Report. Included is the search for answers to questions raised in that report. A cooperative program on phase identification was initiated in late March with Professor H. F. W. Taylor.

The 7% Al_2O_3 substituted tobermorite which showed improved properties gave excessive shrinkage at 350°C , casting doubt on its usefulness at the elevated temperatures of geothermal wells. The results, however, indicated that Class J cement (designated cement J) modified to compositions of 1.0 C/S by addition of $\text{Ca}(\text{OH})_2$ and to composition of 0.65 C/S+A by addition of silica and Al_2O_3 merited development.

Class G cement (designated cement G) plus 40% silica in weight ratio of 71:29 performed satisfactorily in normal weight slurries, but development of equilibrium phases particularly in the presence of excess silica originating from the formation or additions such as fly ash raised some questions. Longer periods of curing at the elevated temperature will be required for full evaluation. The effects of slurry weight reducing additions are being determined on both cement G and cement J.

Mix Materials

Cement G and silica are of quality used in cementing operations, and were supplied by Halliburton. The other materials, also used in field operations and/or experimentation, were supplied by Dowell. Alumina was introduced as gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, or infrequently, as kaolin. The Fe_2O_3 was added as goethite, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Results

Cement J at 1.0 C/S composition plus additions

Earlier results indicated that xonotlite (1.0 C/S composition) might not be a satisfactory binder because of the relatively high absolute density of this phase. Low strengths were expected and observed in some tests, and computations based on absolute density indicated that xonotlite would have a porosity 11% higher than tobermorite.

The results on cement G at 1.0 C/S showed xonotlite as binder and very high strengths. The 0.6 and 0.8 C/S compositions of cement G also gave high strengths and contained xonotlite as the major binder. The presence of xonotlite at 0.6 and 0.8 C/S was questioned as being a stable phase. Samples of both cement G and cement J autoclaved at 350°C for 7, 30 and 90 days have been submitted to Dr. Taylor for determining shift in the equilibrium with time of curing.

In present tests, cement J was modified to a 1.0 C/S composition and used with additions of Al_2O_3 , Fe_2O_3 , gypsum and NaCl. An extended summary of the results is given in Table 1. Sufficient water was added to provide a pourable slurry (as judged by visual examination). The W/S ratio as weight of water/total weight of all solids is included in Table 1.

Table 1. Cement J adjusted to 1.0 C/S composition and with additions

Additions %				Compressive Strength, psi				
Al_2O_3	Fe_2O_3	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	NaCl	W/S	1d150	7d175	7d250	7d350°C
0	-	-	-	.46	6500	-	-	4400
4	-	-	-	.46	4630	-	-	4300
4	-	-	-	.43	5600	7200	6200	3500
4	2	-	-	.43	6000	7100	6200	3100
4	4	-	-	.43	5500	5500	5200	3200
4	6	-	-	.43	5000	5800	6100	3450
3	1	-	-	.41	6300	5600	6400	4400
3	2	-	-	.43	7900	-	-	-
0	2	-	-	.43	9800	9500	3600	5500
0	4	-	-	.43	7600	8700	4000	5250
3	-	4.3	-	.44	5350	4000	5950	2550
3	-	-	2.0	.44	4100	3100	4350	2250
(4% perlite, 2% bentonite)				.44	5350	4000	5950	2550

In all tests, the 1d-150°C strength was generally high to very high, and was affected by kind and amounts of addition. The 7d-175°C strength ranged from lower to higher than the 1d-150°C strength. The 7d-250°C strengths varied only moderately from the 175°C results, except for the 2 and 4% Fe_2O_3 products which showed a relatively high loss. All products at 350°C have much lower strengths than at 250°C except the 2 and 4% Fe_2O_3 samples which showed a substantial increase.

Among the effects of the individual additions on strength, that of Fe_2O_3 is striking in giving high strength at 150 and 175°C. Alumina

alone did not have this effect; also, additions of 2 to 6% Fe_2O_3 to a 4% Al_2O_3 mix yielded effects similar to that of Al_2O_3 alone. The 4.3% gypsum (2.0% SO_3) addition with 3% Al_2O_3 lowered strength at all temperatures, particularly at 350°C. The effect of 2% NaCl was even worse. The 4% perlite - 2% bentonite addition (without increased water content) did not cause a significant strength decrease at 150°C but caused variable decreases at the other temperatures with that at 350°C being among the largest.

Cement J at 0.60 and 0.65 C/S+A

The 0.6 C/S composition being that of truscotite had been included in many tests. It tended to have low early strength with Al_2O_3 additions, but other satisfactory properties. As more data were developed, the composition was increased to 0.65 C/S with Al_2O_3 additions of 2 to 5%.

Representative results, some showing variability in series of tests and in duplicate tests, are compiled in Table 2. The overall results show that the strengths were satisfactory with the results on the 3 and 4% Al_2O_3 mixes at 0.65 C/S generally being somewhat better. The strengths of these compositions at 350°C were higher than of the 1.0 C/S cement J products.

The maximum recommended additions of perlite (1 cubic foot per sack of cement, 8% by weight) were used with and without 2% bentonite. Both additions to 3 and 4% Al_2O_3 - 0.65 C/S compositions gave very low strengths in the 1d-150°C cure due largely to the segregation of the perlite to the surface of the specimen. The other strengths tended to be low down to the range of 1000 psi at 350°C.

Table 2. Cement J compositions at 0.6 and 0.65 with Al_2O_3 at 0 to 5 %

C/S	Al_2O_3 %	W/S	Compressive Strength, psi at Temperature			
			1d-150°C	7d-175°C	7d-250°C	7d-350°C
0.6	0	.37	4300	8350	6500	6500
0.6	0	.41	4150	6200		
0.6	2	.41	2500	4950		
0.6	4	.41	6000	9800		
0.6	5	.37	-	8100	8500	4600
0.6	6	.41	3000	8050		
0.65	2.5	.37	2250		6550	
0.65	3.0	.37	2600		8750	
0.65	3.5	.37	3750		7000	
0.65	4.0	.37	4200		7250	
0.65	3	.37	5100	8600	9700	4600
0.65	3	.37	3350	10150	9150	4300
0.65	4	.37	4650	10750	11200	5700
0.65	4	.37	3500	10150	10300	5350
0.65	3 ⁽¹⁾	.49	0	2300	1000	1200
0.65	4 ⁽¹⁾	.49	0	2000	1700	950
0.65	3 ⁽²⁾	.49	0	1600	1800	950
0.65	4 ⁽²⁾	.49	0	1800	2000	1000

(1) 8% perlite added by weight of mix; (2) 8% perlite and 2% bentonite added

Effects of perlite, perlite plus bentonite and fly ash on strength

Before presenting the strength results, some tests and results on the reactivities of the three additions with BC_2S are as follows. Mixes of BC_2S and additions in weight ratios of 64:36 were slurried with

water to yield a pourable mix and autoclaved at 175 and 250°C for 1 and 7 days at each temperature. The mix proportions were selected to yield a C/S+A ratio of approximately 0.8 with tobermorite as the potential reaction product. All products were examined by X-ray diffraction. The bentonite reacted completely in 1d at 175, the product being well crystallized tobermorite.

The perlite apparently inactivated the BC_2S through 7 days at 175°C and 1d at 250°C. After 7 days at 250°C well crystallized tobermorite was detected as major phase. The fly ash - BC_2S showed no reaction product at 1 day at 175°C, a small amount of tobermorite at 3d and a moderate amount at 7 days. At 250°C small and large amounts of tobermorite were detected after 1 and 7 days, respectively.

The strength results given in Table 3 were determined at 3 W/S ratios on cements J and G with additions. Discussions refer only to the highest W/S which yielded a pourable slurry. Only the 1d-150°C and 7s-175°C strengths are reported; those at 250°C and 350°C appeared sufficiently high but were more variable than in the other cements of this study. The variability may have been due to different extents of the separation of the perlite.

The strengths of cement G with perlite and perlite plus bentonite at W/S of 0.43 were low at the low temperatures. The results for cement J were higher. The larger variability of the results for both cements than expected may reflect non-uniformity in distribution of the perlite. The tests including some modifications are being repeated.

Table 3. Effect of perlite and perlite plus bentonite on compressive strengths of class G and class J cements at different W/S ratios

Compressive strengths of 1.0 C/S class G cement						
W/S:	5% Perlite			4% Perlite + 1% Bentonite		
	<u>.26</u>	<u>.34</u>	<u>.43</u>	<u>.26</u>	<u>.34</u>	<u>.43</u>
1d-150	3350	1150	600	2800	1600	750
7d-175	3600	1700	850	3950	3200	1300

Compressive strengths of 0.85 C/S class J cement						
W/S:	5% Perlite			4% Perlite + 1% Bentonite		
	<u>.28</u>	<u>.37</u>	<u>.46</u>	<u>.28</u>	<u>.37</u>	<u>.46</u>
1d-150	1950	1700	1100	2150	2000	1450
7d-175	3500	3450	2850	3850	3400	3450

Compressive strength of 56 class G: 44 Fly ash			
W/S:	<u>.28</u>	<u>.34</u>	<u>.41</u>
2d-23 ⁰ C	4000	1750	750
7d-175 ⁰ C	9400	9100	5350
7d-250 ⁰ C	7000	4700	3100
7d-345 ⁰ C	4600	3200	2250

Similar tests were conducted with cement G and fly ash (56 G: 44 fly ash, 1 sack of cement to 1 cu. ft. of fly ash) and the results are included in Table 3. The precure was for 2d at 23⁰C instead of the 1d-150⁰C used previously with cement G. (This was done to avoid formation of α C₂SH and CSH(1) as the initial product which was suspected of having a delayed effect on the binders at the higher temperatures.) The results

show the same general variations in strength with curing cycles as shown by cement J, particularly the large strength decrease at 350°C.

Table 4. Comparison of 23°C and 150°C precure on cement G with and without perlite and bentonite

	Cement Composition			
	Cement G+S	Cement G+S	Cement G+S + 5% Perlite	Cement G +S 4% Perl. + 1% Ben.
Precure:	23°C	23°C + 150°C	23°C	23°C
Temp. :	Strength, psi			
1d-23°C	500		275	350
1d-150°C	-	1850	-	-
7d-250°C	8800	8650	3150	4600
7d-350°C	10000	9750	4450	4500

The effects of the 23°C and 150°C precure of cement G + silica at 1.0 C/S with and without addition of perlite and perlite plus bentonite at 0.37 W/S are shown in Table 4. The 1d-23°C precure followed by 1d at 150°C gave a strength of 1850 psi not significantly lower than observed previously (Third Quarterly Report) of 2400 psi. The 250°C and 350°C strengths were the same for both precures and only slightly lower than observed previously. There was no decrease in strength going from 250 to 350°C. The mixes with perlite and perlite plus bentonite showed a strength of 4450 and 4500 psi at 275 and 350°C, respectively, which is an increase for the perlite mix, going from 275 to 350°C, and

negligible decrease for the perlite plus bentonite mix.

Volume changes in water at elevated temperatures

At present, linear change tests are underway on bars of 11 cements. The results at 250°C for 7 days are given in Table 5 along with the compositions of the cements.

Table 5. Linear changes of cements in water
for 7 days at 250° C

<u>Class Cement</u>	<u>Composition</u>	<u>Addition</u>	<u>Linear Change %</u>
G	71G:29S	none	+0.100
G	"	5% Perlite	+0.020
G	"	4% " + 1% Bent.	+0.016
G+F.A.	56G:44 F.A.	Fly ash	+0.048
J	1.0 C/S	3% A.	+0.031
J	1.0 C/S	3% A + 2% NaCl	-0.032
J	1.0 C/S	3% A + 4.3% Gyp.	-0.052
J	0.65 C/S	2.5% Al ₂ O ₃	+0.049
J	"	3.0% "	+0.051
J	"	3.5% "	+0.024
J	"	4.0% "	+0.029

Cement G plus 40% silica (71G:29S) expanded 0.100% in fair agreement with the 0.075% observed previously. Additions of perlite and perlite plus bentonite reduced the expansions to 0.020 and 0.021 percent, respectively. Fly ash, 1 cubic foot per sack of cement, (56G:44F.A.)

reduced the expansion to 0.048%.

Cement J, at 1.0 C/S plus 3% Al_2O_3 , expanded to 0.031 %, substantially higher than the previous value of -0.002% of the same composition without Al_2O_3 . Additions of 2% NaCl and 4.3% gypsum (2.0% SO_3) caused shrinkages of 0.032 and 0.052%, respectively. Cement J at 0.65 C/S with additions of Al_2O_3 showed average expansions of 0.050% at 2.5 and 3.0% Al_2O_3 and 0.027% at 3.5 and 4.0% Al_2O_3 , respectively.

Cement-steel bond strengths

The specimen assemblage for bond strength consisted of a 3/4 inch dia. by 2 inch mild steel rod, centered in a 2 inch dia. by 1 inch high container. The cement slurry was placed around the rod and cured for 1 d at 150°C. After an additional curing at 250°C for 7d, the steel rod was loaded in a compression tester to failure of the bond.

The data for one set of specimens, along with cement compositions, are given in Table 6. Total loads for each specimen and averages are given. Duplicate loads were in good agreement for 3 of the 4 cements; the fourth showed a sizeable difference. The shear stress in psi is reported for the average loads. These are very high shear stresses, and a possible explanation is based on the expansion of the cements under the restrained condition of test. The unrestrained expansions and the kind of binder are given at the bottom of Table 6.

The compressive stress developed in the restrained cement due to expansion would increase the steel-cement bond. The binders, with the exception of xonotlite, gave approximately the same bond with the steel. The question is raised if xonotlite, in spite of high compressive stress in the cement, is a weaker bonding cement to steel than the other phases.

Table 6. Cement-formation bond strength

Cement:	0.85 C/S J	G	0.65 C/S J	0.65 C/S+3A
	Load to break bond, lbs.			
	5000	2500	4800	4800
	5450	2500	3350	4700
Average load:	5225	2500	4075	4750
Shear stress, psi:	2210	1060	1730	2010
Exp. of cement at 250°C:	0.075	0.100	0.070	0.050
Binder:	Gyrolite + Scawtite	Xonotlite	Gyrolite + Scawtite	Tobermorite

Cement-formation bonds

The same assemblage is being used in measuring the cement-formation bond as in the cement-steel bond test, a cylindrical specimen of the formation replacing the iron bar. The tests are underway with granite and sandstone assemblages.

It is recognized that the bond between cement and formation consists of mechanical interlocking of the cement with the irregular surface of the rock and chemical bonding. Considering the complexity of such bond and attempted testing of a fragile rock, it was considered desirable to resort to simple measurement of the compressive strength of cubes made of rock fines and cements. The fines (passing a 20 mesh sieve and retained on a 100 mesh sieve) were prepared as slurries in 50:50 weight ratio with the cement and cured following cycles used in the other tests.

Table 7. Strengths on formation fines and cements J and G
(values in parentheses are for duplicate runs)

<u>Formation fines</u>	<u>Time & Temp.</u>	<u>Compressive Strength, psi</u>	
		<u>Cement J</u>	<u>Cement G</u>
Granite	1d-150 ⁰ C	2550	4250
"	7d-175 ⁰ C	3950	3000
"	7d-250 ⁰ C	4300	6800
"	7d-350 ⁰ C	2400	4400
Sandstone	1d-150 ⁰ C	3100	5600
"	7d-175 ⁰ C	3450	5950
"	7d-250 ⁰ C	4600	2800
"	7d-350 ⁰ C	2300	2750
Dolomite	1d-150 ⁰ C	1900	2000
"	7d-175 ⁰ C	2600	1100
"	7d-250 ⁰ C	4350	1850
"	7d-350 ⁰ C	2050	3500
Shale (A)	1d-150 ⁰ C	2500 (2450)	1550 (1450)
"	7d-175 ⁰ C	2850 (3200)	1000 (950)
"	7d-250 ⁰ C	4000 (3100)	1250 (1300)
"	7d-350 ⁰ C	2300 (3450)	2000 (1600)
Shale (B)	1d-150 ⁰ C	1350	2800
"	7d-175 ⁰ C	4200	2450
"	7d-250 ⁰ C	4900	4850
"	7d-350 ⁰ C	1800	2750

Results on granite, sandstone, two shale and dolomite fines with cements G and J are compiled in Table 7. The strengths show minor to significant differences for the two cements with a single aggregate.

Generally the strengths at all temperatures appear adequate with some question of Shale A-cement G results. The strengths were significantly lower than those with cement J. The tests were repeated with both cements, and the results are listed in parentheses in Table 7. The close duplication of the results with cement G indicates the finding is factual. The tests were repeated with another shale designated Shale B in Table 7. No comparable weakness was found with this shale. These results tend to confirm experiences encountered with variations in shale qualities in actual drilling operations.

More complete data on the formation-bond strength tests giving consideration to the induced compressive strength or shrinkage of the cement and type of binders are required. These tests as mentioned are underway with available supply of rocks. (Difficulty is being experienced in obtaining rocks of sufficient size.)

Discussions

The results during the fourth quarter are helping to define the problem of possible malfunctioning of cements at elevated temperatures. Strength used as a single criterion of quality in screening tests in the laboratory has limitations. The classical example of portland cement cured at temperatures below about 120°C to form $\alpha\text{C}_2\text{SH}$, a binder of very low strength, illustrates the need to relate strength to kind of binder.

Dowell reported that cements of low C/S (excessive amount of silica and fly ash) cured at 316°C for prolonged time underwent strength retrogression. They reported formation of a truscotitte-type binder. Results at CSM confirmed the relative low strength of truscotitte or truscotitte-

gyrolite intergrowth. Using portland and perlite both of which contribute K_2O , the binder may be reyerite, a K_2O -containing mineral similar to truscotitte. Some of the strengths for a truscotitte composition using normal weight slurries at about 3000 - 3400 psi, as reported in the Third Quarterly Report (CSM), would appear satisfactory. The effect of additions, particularly perlite and fly ash, merit further study to expand the findings reported by Dowell.

The effect of spontaneous expansion and shrinkage of the cement at the elevated temperatures of geothermal wells may relate significantly to the formation-cement and steel-cement bonds.

Appendix 3

BNL Contract 418691-S
Phosphate Bonded Glass Cements
for Geothermal Wells

Quarterly Technical Report No. 3
January to March, 1978

from

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1. Introduction

This report covers the highlights of the work completed under contract BNL 418691-S during the third quarter of work from January 1, 1978 to March 31, 1978. The five major areas of concentration during this quarter and a discussion of their relevance to geothermal cementing are given below.

1. Reactions at 200°C in the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. In order to design a high temperature cement which will be stable under geothermal conditions, the reactions leading to stable cementing phases must be understood. The aluminum phosphate cements are known for their high temperature resistance (Ref.1). Indeed, at least one patent has been issued for the use of aluminum phosphate cement as a well completion materials. The findings suggest that the cement is compatible with drilling muds and resists filtration (Ref.2).

Our findings suggest that if an aluminous material is mixed with phosphoric acid and emplaced at a temperature of 200°C, a reaction would take place to form aluminum phosphate and an aluminum hydroxide. This reaction might cement an aggregate at geothermal conditions. Further, as the above reaction proceeded in situ between the casing pipe and the wall rock, the corrosive acid will be converted to virtually pure water. These findings are extremely encouraging and suggest a real potential for phosphate cement in geothermal applications.

2. Reactions at 200°C in the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$. Calcium phosphates play an important role in the cementing of glass-

phosphate cements (Ref. 3). The results presented below show that a lime containing material reacted with phosphoric acid at 200°C will yield calcium hydroxide and calcium acid phosphate or hydroxapatite. This reaction could also be a cementing reaction and also neutralizes the phosphoric acid so that corrosion may not be a problem. The precipitation of calcium hydroxide is a significant observation as this phase is known to be stable at geothermal conditions (Ref. 4) and is an important cementing phase in the more widely used portland type cements. These data will also be used in designing a phosphate cement for geothermal well completion.

3. Reactions at 200°C in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. This work is just beginning. It will lead to an understanding of the interactions of phosphoric acid with calcium aluminates and those compositions showing the most favorable reactions will be used for experimental cements.

4. Glass-phosphoric acid interactions. Since the goal of this project is to design a glass frit which will react with phosphoric acid to form a cement, an understanding of the interactions are necessary. Very little information is available on the corrosion of glass by liquids (Ref.5) and nothing is available on phosphoric acid attack. The work of Sanders and Hench has shown that ions are extracted from glass surfaces and can alter the surface compositions (Ref.6).

The results below indicate that in a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$

glass the silica concentration controls the rate of attack by a 30% phosphoric acid. By controlling silica content, the setting time of a phosphate-glass cement can be controlled by controlling the leach rate of Calcium and Aluminum ions from the glass.

5. Stability of existing phosphate cements at geothermal conditions. Small cylinders of commercially available phosphate cements have to be mixed, set and placed in water and brine at 200°C. Initial tests show considerable interaction of the cement with the solutions and deterioration of strength but the cement is not totally disintegrated. While these observations offer some encouragement, improvements must be made if long term stability in a geothermal environment is to be achieved.

2. Results:

1. Reactions at 200°C in the System $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$.

In the last quarterly report, the 200°C isothermal section for the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ was discussed at length. Table 1 lists the firings made during this quarter. Figure 1 shows the isothermal section of the ternary. All runs were made at 200°C.

The procedure used was described in the previous quarterly. One change was made. A thicker walled Pyrex (trademark-Corning Glass) glass tubing is now used for all reaction ampoules. This change was necessitated by an explosion of a softer glass tubing ampoule which destroyed about 30 samples. Since the change in materials, no difficulties have been encountered with the technique.

The stability limits of the solution phase have been defined in the high phosphate region. The primary phase in this region has not yet been identified. The identification is somewhat complicated by room temperature hydration of the phosphate rich phase. If alumina is added to phosphoric acid over the range of dilute acids to highly concentrated acid and the mixture is heated to 200°C, the first reaction will be the precipitation of AlPO_4 . As this takes place, the acid will be neutralized. Continued reaction will lead to the co-precipitation of an aluminum hydrate of the AlOOH type. The exact nature of this phase at 200°C has not been determined.

Runs are continuing to clear up the undefined relationships. Some of the fine points may not be resolved but the basic

Table 1

Firings Made In The System Al_2O_3 - P_2O_5 - H_2O

Run#	Initial Composition Wt%			Reaction Time (hrs)	Final Phase
	Al_2O_3	P_2O_5	H_2O		
35	1.93	63.51	34.56	24	LIQ+VAP
36	3.86	65.42	30.72	57	LIQ+VAP
37	5.80	67.32	26.88	177	Solid+LIQ+VAP
38	7.73	69.23	23.04	177	Solid+LIQ+VAP
39	9.66	71.14	19.20	177	Solid+LIQ+VAP

Figure 1. Tentative 200°C isotherm for the system
 Al_2O_3 - P_2O_5 - H_2O

data necessary for cement design has been achieved.

2. Reactions at 200°C in the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$.

The phase relations in this system are being studied using the pyrex ampule technique described for the alumina system. Calcium oxide is being used as a starting material for most runs and tricalcium phosphate is being used to confirm some of the findings.

Table 2 lists the phases observed at 200°C. Figure 2 shows the compositions of the experiments made and Figure 3 shows the phase equilibria for the 200°C isothermal section.

Three solid phases have been observed, hydroxylopatite, calcium acid phosphate, CaHPO_4 , and monocalcium phosphate monohydrate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ which is the 1.1.3 compound. Calcium hydroxide has not been observed as yet but there is considerable evidence that it is a stable phase at these conditions. This acid phosphate phase precipitates as extremely well formed single crystals as shown in Figure 4. The monohydrate forms as a much finer white crystalline precipitate. Several runs were made in which the final phase was a single solution but in cooling to room temperature the monohydrate crystallized. As indicated by the two phase tie lines, an acid phase (up to 45 percent P_2O_5) when mixed with lime will yield the calcium acid phosphate phase as a precipitate. As these crystals grow the composition of the acid will shift to virtually pure water. A schematic of the changes in solution is shown in Figure 5. This diagram is intended to show shifts in solution with extremely small concentration of

Table 2-Phases Observed in System $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ at 200°C

No.	Initial Composition %			Reaction Time day + hr	Final Phases
	CaO	P_2O_5	H_2O		
1	1	4.95	94.05	20d 9hr	$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
2	2	4.9	93.1	20d 9hr	$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
3	3	4.85	92.15	20d 9hr	$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
4	4	4.8	91.2	20d 9hr	$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
5	5	4.75	90.25	19d 10hr	$\text{CaHPO}_4 + \text{HA}^* + \text{LIQ} + \text{VAP}$
6	1	9.9	89.1		$\text{LIQ} + \text{VAP}$
7	2	9.8	88.2		$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
8	3	9.7	87.3		$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
9	4	9.6	86.4		$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
10	5	9.5	85.5	16d	$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
11	1	19.8	79.2		$\text{LIQ} + \text{VAP}$
12	2	19.6	78.4		$\text{LIQ} + \text{VAP}$
13	3	19.4	77.6		$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
14	4	19.2	76.8		$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
15	5	19.0	76.0	14d	$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
16	1	29.7	69.3		$\text{LIQ} + \text{VAP}$
17	2	29.4	68.6		$\text{LIQ} + \text{VAP}$
18	3	29.1	67.9		$\text{LIQ} + \text{VAP}$
19	4	28.8	67.2		$\text{LIQ} + \text{VAP}$
20	5	28.5	66.5	9d 3hr	$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
21	10	27.0	63.0	6d 18hr	$\text{CaHPO}_4 + \text{LIQ} + \text{VAP}$
22	5	38.0	57.0	14d	$\text{LIQ} + \text{VAP}$
23	6	37.6	56.4		$\text{S} + \text{LIQ} + \text{VAP}$
24	7	37.2	55.8		$\text{S} + \text{LIQ} + \text{VAP}$
25	8	36.8	55.2		$\text{S} + \text{LIQ} + \text{VAP}$
26	9	36.4	54.6		$\text{S} + \text{LIQ} + \text{VAP}$
27	5	47.5	47.5	9d 5hr	$\text{LIQ} + \text{VAP}$
28	6	47.0	47.0		$\text{LIQ} + \text{VAP}$
29	7	46.5	46.5		$\text{S} + \text{LIQ} + \text{VAP}$
30	8	46.0	46.0		$\text{S} + \text{LIQ} + \text{VAP}$
31	10	45.0	45.0	9d 5hr	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{LIQ} + \text{VAP}$

*HA = Hydroxylapatite

Figure 2. Compositions of firings made in the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$

Figure 3. The 200°C isotherm for the system
CaO-P₂O₅-H₂O

Figure 4. Single crystals of calcium acid phosphate grown in phosphate solution. Length = 0.8mm

Figure 5. Schematic diagram showing the phase relations in the "pure" water region

calcium ion and phosphate. As more lime is dissolved hydroxylapatite will begin to precipitate and the solution will become basic. Additional runs are being made in this system and determinations at 200°C will be completed during the next quarter.

3. Reactions at 200°C in the System $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$.

Having determined the major reactions of phosphoric acid with lime and alumina, we are beginning runs on reactions of phosphoric acid with calcium aluminates. The first series will be made using 50% mixtures of the two oxides. The attempt is to discover if any calcium alumino phosphate hydrates are stable at 200°C and if they will behave as cementing phases. The pyrex ampule method is being used. Initial results show that the 30% P_2O_5 phosphoric acid dissolves 1% of the $\text{CaO}/\text{Al}_2\text{O}_3$ mixture. At 2% AlPO_4 is the stable phase and at 10% two phases are in equilibria with the $\text{Ca}^{++}/\text{Al}^{+++}$ containing phosphate solution. One of the phases is AlPO_4 and the other is probably crandallite, $\text{CaAl}_2(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ which has an alunite structure.

4. Interactions of Glass with Phosphoric Acid.

In order to control the set time of a phosphate cement a knowledge of the interaction between phosphoric acid and a Calcium and Aluminum containing glass is essential. In the last quarterly report, the procedure for drawing fibers of various silicate glasses containing equal amounts of CaO and Al_2O_3 was presented. The fibers, with a measured surface area, are exposed

to 30% H_3PO_4 solution and the weight change is measured as a function of time.

Table 3 lists the results obtained to date on this phase of the investigation. Figures 6-11 show the data plotted on weight loss per unit surface area vs. time graphs.

All of the curves with the exception of Figure 10 show a common feature. After initial weight loss, the fibers begin to regain some of the lost weight. In one case, an actual weight gain has been observed. The exact mechanisms leading to this behavior are not yet fully understood but we believe the initial loss is due to leaching of Ca^{++} and Al^{+++} . This leaves a silica gel layer on the surface after a finite amount of time. This phase acts as a host into which phosphate counter diffuses leading to a precipitation of calcium alumino-phosphates on the fiber surface.

Other conclusions to be drawn from the data are that the 55% SiO_2 glass is severely deteriorated by the phosphoric acid at slightly elevated temperatures; the 65% SiO_2 glass shows extremely little interaction with phosphoric acid, even at 140°C , and finally that the 57% SiO_2 glass shows considerable interaction without catastrophic deterioration.

5. Stability of Available Phosphate Cements.

Many of these firings were lost in the March explosion of the ampules and therefore only two data points are available. The phosphate cement used in this test was a standard dental glass

TABLE 3

Weight Change Data For Glass Fibers
Reacted With Phosphoric Acid

65 wt/% SiO_2 Glass
40°C
30% H_3PO_4 Solution

Sample: G_4

Fiber No.	Time	Loss in Wt (gms)	Surface Area (cm^2)	$\frac{\text{Loss in Wt (gms)}}{\text{Surface Area (cm}^2\text{)}}$
G_{41}	10 mins	0.0008	2.27	3.52×10^{-4}
G_{42}	30 mins	0	2.06	0
G_{43}	1 hr.	0.0003	3.81	0.79×10^{-4}
G_{44}	2 hrs.	0	1.97	0
G_{45}	4 hrs.	0.0006	2.45	2.45×10^{-4}
G_{46}	8 hrs.	0.0006	2.43	2.47×10^{-4}
G_{47}	16 hrs.	0.0008	2.23	3.58×10^{-4}
G_{48}	32 hrs.	0.0007	3.79	1.85×10^{-4}
G_{49}	64 hrs.	0.0001	3.19	0.31×10^{-4}
G_{410}	128 hrs.	0.0019	2.49	7.6×10^{-4}

55 wt/% SiO_2 Glass
40°C
30% H_3PO_4 Solution
Sample: G_6

G_{61}	10 mins	0	0.5368	0
G_{62}	30 mins	0.0007	0.7055	0.99×10^{-3}
G_{63}	1 hr.	0.0011	0.6347	1.7×10^{-3}
G_{64}	2 hrs.	0.0024	0.5284	4.5×10^{-3}

TABLE 3 (cont.)

55 wt% SiO₂ Glass
 40°C
 30% H₃PO₄ Solution
 Sample: G₆

Fiber No.	Time	Loss in Wt. (gms)	Surface Area (cm ²)	Loss in Wt (gms) Surface Area (cm ²)
G ₆₅	4 hrs.	0.0051	0.6362	8.02×10^{-3}
G ₆₆	8 hrs.	0.0137	1.100	12.4×10^{-3}
G ₆₇	16 hrs.	could not be weighed	0.686	-
G ₆₈	32 hrs.	0.0105	1.126	9.3×10^{-3}
G ₆₉	64 hrs.	0.0089	1.075	8.2×10^{-3}
G ₆₁₀	128 hrs.	could not be weighed	0.720	-

65 wt% SiO₂ Glass
 90°C
 30% H₃PO₄ Solution
 Sample: G₄

G ₄₁	10 min.	0	2.039	0
G ₄₂	30 min.	0	2.254	0
G ₄₃	1 hr.	0.0003	2.52	1.19×10^{-4}
G ₄₄	2 hrs.	0.0003	3.824	0.784×10^{-4}
G ₄₅	4 hrs.	0.0004	2.014	1.99×10^{-4}
G ₄₆	8 hrs.	0.0003	2.538	1.18×10^{-4}
G ₄₇	16 hrs.	0.0004	2.035	1.97×10^{-4}
G ₄₈	32 hrs.	0.0001	1.77	0.57×10^{-4}
G ₄₉	64 hrs.	0	2.41	0
G ₄₁₀	128 hrs.	0	2.337	0

TABLE 3 (cont.)

57 wt% SiO₂ Glass
40°C30% H₃PO₄ SolutionSample: G₈

Fiber No.	Time	Loss in Wt(gms)	Surface Area (cm ²)	$\frac{\text{Loss in Wt (gms)}}{\text{Surface Area (cm}^2\text{)}}$
G ₈₁	10 min.	0	1.612	0
G ₈₂	30 min.	0.0001	1.246	0.8025×10^{-4}
G ₈₃	1 hr.	0	1.458	0
G ₈₄	2 hrs.	0.0001	0.837	1.19×10^{-4}
G ₈₅	4 hrs.	0.0002	1.752	1.14×10^{-4}
G ₈₆	8 hrs.	0.0001	1.01	0.988×10^{-4}
G ₈₇	16 hrs.	0.0002	1.645	1.21×10^{-4}
G ₈₈	32 hrs.	0.0006	1.168	5.1×10^{-4}
G ₈₉	64 hrs.	0.0006	1.954	3.07×10^{-4}
G ₈₁₀	128 hrs.	0	2.903	0

TABLE 3 (cont.)

55 wt% SiO₂ Glass
90°C
30% H₃PO₄ Solution

Sample: G₆⁹

Fiber No.	Time	Loss in Wt (gms)	Surface Area (cm ²)	Loss in Wt (gms) Surface Area (cm ²)
G ₆₁ ⁹	10 min.	0.0003	1.115	0.269 x 10 ⁻³
G ₆₂ ⁹	30 min.	0.0021	0.8643	2.43 x 10 ⁻³
G ₆₃ ⁹	1 hr.	0.0140	1.2188	11.49 x 10 ⁻³
G ₆₇ ⁹	20 min.	0.0012	1.303	0.921 x 10 ⁻³
G ₆₈ ⁹	40 min.	0.0072	1.352	5.33 x 10 ⁻³
G ₆₉ ⁹	80 min.	0.0082	2.1835	3.76 x 10 ⁻³
G _{6,10,1} ⁹	50 min.	0.0068	0.910	7.47 x 10 ⁻³
G _{6,10,2} ⁹	50 min.	0.0075	0.824	9.10 x 10 ⁻³
G _{6,10,3} ⁹	50 min.	0.0092	1.017	9.05 x 10 ⁻³
G _{6,10,4} ⁹	50 min.	0.0091	0.965	9.43 x 10 ⁻³
G _{6,10,5} ⁹	50 min.	0.0136	1.544	8.81 x 10 ⁻³

55 wt% SiO₂ Glass
140°C
30% H₃PO₄ Solution
Sample: G₆¹⁴

G ₆₁ ¹⁴	10 min.	0.0151	1.797	8.4 x 10 ⁻³
G _{6,2,1} ¹⁴	5 min.	0.0207	1.502	13.785 x 10 ⁻³
G _{6,2,2} ¹⁴	5 min.	0.0008	0.677	10.03 x 10 ⁻³

Figure 6. 57% SiO₂ glass 40°C, 30 wt% H₃PO₄ sol.

Figure 7. 55 wt% SiO_2 glass 90°C , 30% H_3PO_4 sol.

Figure 8. 55 wt% SiO_2 glass 40°C , 30 wt% H_3PO_4 sol.

Figure 9. 55 wt% SiO₂ glass 140°C, 30% H₃PO₄ sol.

Figure 10. 65 wt% SiO_2 glass 40°C , 30 wt% H_3PO_4 sol.

Figure 11. 65 wt% SiO₂ glass 90°C, 30 wt% H₃PO₄ sol.

bonded phosphate referred to in the dental industry as a silicate cement. Small cylinders of this material were set and sealed in distilled water and a 25% brine solution and heated at 200°C.

After one week some flocculant precipitate formed around the cylinders. After 17 days the cylinders were removed. They did maintain their form although they appear to have lost considerable strength and developed some porosity. Many more runs are being made and will be reported on during the next quarter.

Future Plans

During the next quarter, we will attempt to achieve the following goals:

1. Completion of the 200°C isothermal section for the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$.
2. Completion of the 200°C isothermal section for the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$.
3. Completion of the phosphoric acid corrosion studies on the 21.5 CaO: 21.5 Al_2O_3 : 57^{wt}% SiO_2 glass and the 20.5 CaO: 20.5 Al_2O_3 : 59^{wt}% SiO_2 glass.
4. Completion of strength deterioration studies on phosphate cements after exposure to 200°C water and brine.
5. Begin collecting data at 200°C on the interaction of phosphoric acid with calcium aluminates.

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Appendix 4

DEVELOPMENT OF GEOTHERMAL WELL COMPLETION SYSTEMS

Phase II: Progress Report No. 1
October, 1977 - March, 1978

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Introduction

Dowell's contract with the Department of Energy (DOE) calls for the completion of two phases of work: (1) Phase I - definition of problems and development of equipment and test procedures, and (2) Phase II - actual development of a suitable geothermal cementing system. Phase I has been essentially completed as was reported in our report number C00/4190-1.⁽¹⁾ Certain portions of the Phase I program are still continuing such as equipment design and fabrication and scheduling of field test programs. These should be completed before the end of the next reporting period. Phase II work has been organized and is progressing in the following manner: (1) initial "spearhead" testing, (2) placement measurements, (3) stability measurements, (4) chemical studies, and (5) development of non-Portland systems. This report will cover progress in each of these areas.

Initial "Spearhead" Testing

Our Phase I report included a section entitled "Initial Test Program" and an accompanying flow-chart detailing the plan of attack to be used in our study. In order to minimize the number of samples to be run through this program, pre-testing was done to establish the best candidates. Table I gives a summation of the systems tested and is broken down by slurry weight. For sake of brevity, only the extenders used are listed and not their concentrations in each case. Samples were set at 120°C for one day and compressive strengths measured. Strengths were measured again after 3 days at 325°C. Lightweight cements were run since most operators responding to our survey indicated an interest in this type of system.

In general, the work represented in Table I showed that Portland cements stabilized with 35 to 40 percent silica flour combined with various extenders performed as well if not better than any of the other systems tested. Several extenders were used, including: bentonite, perlite, diatomaceous earth, coal, sawdust, and sodium silicate. With most of these extenders, the extra water required with the extender is the agent actually producing the light weight. In many cases, the best strengths were obtained when using an extender which acts as a water thickener such as bentonite or sodium silicate. Extender to water ratio had to be controlled carefully to obtain the best strengths.

Other systems showing promise included Class J cement, silica/lime mixes, and, to some degree, fly ash or other pozzolans with lime. In each case, the calcium to silica (C/S) ratio was the same as that obtained in the Portland/silica systems discussed above--0.8 to 1.0. It is interesting to note that silica/lime blends with other than the 0.8 to 1.0 C/S ratio produced lower strengths--especially those with higher calcium ratios. These will be dropped from further consideration as will any blend which does not perform at least as well as the Portland/silica system.

Careful study of the data in Table I reveals that other failures were recorded in the lightweight systems. Aluminous cements (Fondu and Lumnite) produced lower strengths at 325°C than did the stabilized Portland/silica blend. Using the usual Portland extenders, the extended aluminous cements produced strengths much lower than those of similar Portland systems and these will be dropped. California natural pozzolans (Airox and Basalt) combined with

Portland gave strengths above Portland-fly ash systems at 100°C but much below the fly ash systems at 325°C. The natural pozzolan systems are much more difficult to retard at elevated temperatures and are therefore being dropped.

In addition to the systems shown in Table I, a limited number of liquid sodium silicate (water glass) cements were tested. These had silica filler and metal oxides or acidic agents to set the cement. Those reaching reasonable strengths at 100°C tended to lose strength and expand slightly in 3 days at 325°C. No further testing of these silicate cements is planned.

In summary, the "Spearhead" testing program shown in Table I has been used more or less to rule out those lightweight systems which show little or no promise of providing a suitable geothermal cement. All those systems showing a 3 day compressive strength of at least 500 psi have been moved into the more rigorous testing program described in our last report. Many of these systems have already undergone initial thickening time testing. Preliminary results of these tests will be covered in the next section of this report.

Placement Measurements

Systems found to be suitable candidates in the "Spearhead" testing described earlier are currently undergoing tests to determine the degree of retardation necessary to make them pumpable in a "real-life" situation. Many of these thickening time tests have already been completed and are reported in Table II. All tests were run under simulated down-hole conditions of temperature and pressure according to API Liner Cementing Schedule 30M.⁽²⁾ This schedule is shown in Table III and has been modified to reflect geothermal

conditions of 8,000 ft. total depth with a temperature gradient of 3.4°F/ft. Slurries were prepared as outlined in API Bulletin No. RP 10B.⁽²⁾

Most of the results presented here should be considered preliminary in that they will be used as a guide to outline further tests to determine if the degree of retardation needed can be obtained for a particular system. Results of such further testing will be presented in future reports.

Chemical Studies

A research effort to better understand the kinetics of portland cement hydration and to determine the reactions responsible for strength retrogression upon exposure to high temperatures has begun. Work so far has largely consisted of the evaluation of analytical instrumentation for suitability in Portland cement research. We have determined that an advanced x-ray diffraction system interfaced with a computer for data analysis, best meets our requirements for detailed analysis of portland cement.

The x-ray system which we are tentatively planning to purchase consists of the following:

High power x-ray generator

Cu long fine focus tube

x-ray diffractometer with vertical goniometer

Scintillation detector

Linear amplifier and ratemeter

Pulse height selector

For data reduction, analysis, and automated instrument operation, this system is interfaced with a 28K computer. The detector output is directly fed to the computer; peaks are then identified and output in the form of a teletype listing. A search program containing diffraction data of compounds of interest in cement research can identify and output a listing of the phases present in a sample. This purchase will be made with non-D.O.E. funds as it will also be used by other areas in Dowell R&D.

A series of cement samples were recently analyzed by this system at the Dow Michigan Division in Midland, Michigan. In every case the Midland system gave superior, detailed information. The reported d-spacings are accurate to 0.001 Å. The sensitivity is such that components comprising less than 1% of the total sample can be positively identified; also, quantitative analysis of cement phases is a possibility.

Synthesis of common portland cement phases has been performed to aid in our research. Reference x-ray information can be obtained from these samples and it will also be possible to observe how each phase behaves when exposed to conditions thought to exist in a geothermal environment. Listed below are the phases of interest and instructions for preparation:

Truscottite

C/S = 0.600 $C_3S_5H_x$

Materials: CaO, silicic acid

Autoclaving: 300°C 10 days

Stability Range: 220-325°C

Gyrolite

$$C/S = 0.667 \quad C_2S_3H_x$$

Materials: CaO, silicic acid

Autoclaving: 250°C 10 days

Stability Range: 150-220°C

Pectolite

$$C/S = 0.667 \quad NC_4S_6H_x$$

Materials: NSH₅, CaO, SiO₂

Autoclaving: 250°C 7 days

Stability Range: 200-325°C

Tobermorite

$$C/S = 0.833 \quad C_5S_6H_x$$

Materials: CaO, SiO₂

Autoclaving: 175°C 7 hours to 7 days

Stability Range: 100-150°C

"3.15Å" Phase

$$C/S = 0.833 \quad C_5S_6H_x \text{ (different crystallinity)}$$

Materials: CaO, silicic acid

Autoclaving: 300°C 10 days

Stability Range: Unknown

Xonotlite

$$C/S = 1.00 \quad C_6S_6H_x$$

Materials: CaO, SiO₂

Autoclaving: 300°C 1 hour

Stability Range: 150-415°C

Stainless steel high pressure curing chambers are used to prepare these phases. Anyone interested in obtaining this equipment should contact:

A. R. Kahmann
Chandler Engineering
7707 E. 38th Street
Tulsa, OK. 74145

To summarize, the chemical measurement effort this quarter has essentially consisted of the evaluation and acquisition of equipment and materials necessary to perform the planned research. A thorough research program is planned once the x-ray equipment is installed and operational. Delivery is expected during the third quarter 1978.

Development of Non-Portland Systems

In the area of non-Portland cementing materials, work is currently underway on two separate systems: an acid-catalyzed furfuryl alcohol/filler blend and a phosphate based cement.

About 20 years ago Dowell introduced an aluminum potassium fluophosphate cement to the oil field (U.S. Patent No. 2,868,294).⁽³⁾ This is produced by reacting dried kaolinitic or bauxitic clay containing potassium salts and fluospar with phosphoric acid solution using coal as a filler. It has a density about 13 lb/gal (S.G. = 1.56). It combines low fluid loss and excellent bond strength to pipe and formation. This system has a strength of about 1000 psi in 24 hrs and a ultimate strength of 3000 psi. Recently prepared samples had a bond strength of 100 to 400 psi to greased brass molds and 30 to 100 psi to mud covered cores. This bonding though desirable makes the preparation of test specimens difficult. Originally, this cement

was discontinued because of its increased cost over Portland cement and its incompatibility with Portland slurries. A copy of the patent has been forwarded to Professor Rockett at the University of Rhode Island.

The furfuryl alcohol system may be prepared using several fillers including powdered coal, graphite, Perlite, diatomaceous earth, or silica flour. The coal system has been selected for further study due to its lightweight properties, relative cost, and superior compressive strengths. The furfuryl alcohol/coal system will develop approximately 3000 psi compressive strength and maintain this level for three days at 300°C. Permeability of this system to water is about 0.01 millidarcies.

The next step is the determination of pumpability of the furfuryl alcohol/coal system. Some problems have been encountered since the rubber diaphragms currently in use in our high pressure/temperature consistometers are not stable when contacted with furfuryl alcohol. This instability causes the diaphragm to contact the stirring paddle in the consistometer cup which then gives rise to false viscosity measurements for the furfuryl alcohol system.

In spite of these difficulties, enough preliminary data has been gathered to indicate that further work is needed to determine the proper catalyst to use with the furfuryl alcohol system. Table IV shows that in some cases furfuryl alcohol without a catalyst will not polymerize in less than six hours at 300°F and 5200 psi and that the malic acid concentration used resulted in a too short thickening time. Alternate diaphragm materials are being investigated so that more meaningful data can be collected in the future.

Table I. "Spearhead" Testing. Samples set at 120°C for 24 hours then cured for three days at 325°C. Additive codes are given at the end of the table.

Weight (ppg)	Cement System	Additives			% H ₂ O BWOC	Comp. Strength (psi)	
		1	2	3		Orig.	3 Days
12.9	Fly Ash/23% Ca(OH) ₂	None			56	186	1068
	Class G	DE	SF		120	1170	1022
	Class J	PERL			100	165	508
12.8	Fly Ash/27% Ca(OH) ₂	None			58	140	1812
	Class G	DE	SF		120	965	900
	Fondu-(Aluminous)	BENT	PERL		105	84	21
12.7	1:1-Class G: Fly Ash	BENT	SF	NaCl	106	1254	1431
	1:1-Class G: Fly Ash	BENT	SF		106	627	1120
	Class G	BENT	SF	PERL	151	621	940
12.6	Class G	BENT	SF		114	690	1500
	Class G	DE	SF		125	942	1395
	1:1-Class G: Fly Ash	BENT			225	255	888
	Class G	BENT	SF	PERL	159	604	805
	Class J	BENT			104	188	653
12.5	1:1-Class G: Fly Ash	BENT			245	210	1125
	Class G	SSS	SF		104	940	855
	Class J	DE			104	222	599
	TXI Lightweight	BENT	SF	NaCl	117	760	145
12.4	Class G	PHB	SF		114	655	1155
	Class J	DE	LIME		120	557	614
	Class J	BENT	PERL	NaCl	140	860	569
	1:1-Class G: Fly Ash	BENT			100	714	250
	Fondu (Aluminous)	PERL	BENT		110	50	13
	Fondu (Aluminous)	DE	BENT		120	24	6
12.3	Class G	BENT	SF		163	516	1032
	Class G	ATTA	SF		121	610	950
	Class G	BENT	SF	PERL	172	485	614
	Class G	BENT	SF	PERL	181	554	583
	TXI-Lightweight	BENT	SF		117	900	106
12.2	Class G	BENT	SF	WOOD	120	1314	1456
	Class G	BENT	SF		135	425	1150
	Trinity Lightweight	BENT	SF		120	1705	1020
	Class G	DE	SF	PERL	155	960	955
	Class G	BENT	SF	NaCl	145	395	835
	1:1-Silica: Lime	Al ₂ O ₃		NaCl	95	1060	764
	1:1-Class G: Fly Ash	BENT	SF	PERL	136	745	755
	1:1-Silica: Lime	Al ₂ O ₃			95	1182	415
	Class J	BENT	WOOD		110	518	195

Table I (Cont.)

Weight (ppg)	Cement System	Additives			% H ₂ O BWOC	Comp. Strength (psi)	
		1	2	3		Orig.	3 Days
12.1	Class J	BENT			125	1360	1324
	Class G	SSS	SF	WOOD	120	1130	975
	Class G	SSS	SF	WOOD	109	944	955
	Class J	DE			124	619	673
	Class G	DE	SF	WOOD	125	1200	589
	Lumnite (Aluminous)	DE	BENT		130	50	54
12.0	1:1-Silica:Lime	None			96	1205	1161
	1:1-Silica:Lime	MgO			96	1290	1234
	1:1-Silica:Lime	CaCl ₂			96	1135	915
	1:1-Silica:Lime	NaCl ²			96	1438	817
	1:1-Silica:Lime	MgCl ₂			96	1168	768
	45:55-Silica:Lime	None ²			96	1197	765
	Class G	SSS	SF		122	555	800
	Fly Ash/Ca(OH) ₂	BENT			100	167	667
	Class G	SSL	SF		132	655	635
	Class G	BENT	SF	PERL	193	416	597
	Fly Ash/Ca(OH) ₂	CaCl ₂			285	761	575
	Fly Ash/Ca(OH) ₂	BENT ²			285	207	522
	Class G	BENT	SF		202	574	425
	Class J	DE	LIME	WOOD	225	300	395
	Trinity Lightweight	PERL			122	1344	266
	Class J	BENT	PERL		144	780	243
	Class J	DE	LIME		144	1065	220
	Lumnite-(Aluminous)	BENT	WOOD		120	140	66
	Fondu-(Aluminous)	BENT	WOOD		110	234	63
11.9	Class G	DE	SF	PERL	120	1270	970
	Class G	SSL	SF	WOOD	115	1260	955
	Class G	BENT	SF		135	445	900
	Class G	DE	SF		163	1165	620
	Class G	DE	SF	PERL	185	701	573
	1:1-Class G:Fly Ash	BENT	PERL		130	767	255
11.8	Class G	SSS	SF	COAL	122	590	600
	Class G	SSL	SF	COAL	130	775	465
	Aerox Poz/Ca(OH) ₂	CaCl ₂			115	531	124
	Aerox Poz/Ca(OH) ₂	None ²			115	307	110
	Trinity Lightweight	DE			130	1835	116
	Aerox Poz/Ca(OH) ₂	None			110	247	84
11.7	Class G	SSS	SF	PERL	104	910	880
	Aerox Poz/Ca(OH) ₂	None			120	529	261
	Aerox Poz/Ca(OH) ₂	None			125	650	297

Table I (Cont.)

Weight (ppg)	Cement System	Additives			% H ₂ O BWOC	Comp. Strength(psi)	
		1	2	3		Orig.	3 Days
11.6	Class G	SSL	SF	WOOD	135	557	696
	1:1-Silica:Lime	WOOD			192	545	620
	Class G	DE	SF	PERL	190	1006	552
	1:1-Class G:Fly Ash	BENT	DE		140	765	133
11.5	Class G	SSS	SF	PERL	122	685	690
	1:1-Class G:Fly Ash	BENT	PERL		160	609	226
11.4	Class G	SSL	SF	PERL	130	890	780
	Class G	SSS	SF	PERL	125	675	660
	Class G	DE	SF	PERL	220	826	500
11.3	1:1-Class G:Fly Ash	BENT	DE	PERL	170	570	325
11.2	1:1-Class G:Fly Ash	DE			180	738	425
11.1	1:1-Silica:Lime	DE			127	485	539
	Class G	SSS	SF	PERL	147	560	490
11.0	Class G	DE			216	835	335
10.9	1:1-Silica:Lime	DE			140	435	330
10.8	1:1-Silica:Lime	PERL			113	802	507
	Class G	DE	PERL		246	789	330

Additive CodesCodeMaterial

ATTA

Attapulgite

BENT

Bentonite

COAL

Powdered Coal

DE

Diatomaceous Earth

LIME

Ca(OH)₂

PERL

Perlite

PHB

Pre-hydrated Bentonite

SF

Silica Flour

SSL

Sodium Silicate-Solution

SSS

Sodium Silicate-Solid

WOOD

Sawdust

Table II. Thickening time tests on potential geothermal cementing materials. Additive and retarder codes given at end of table. Time units are hours:minutes.

Cement	Additives (Percent BWOC)						% Water	Retarder		Thick. Time
	Code	Amt.	Code	Amt.	Code	Amt.		Code	Amt. (%)	
Permanente "G"	SAND	35					54	1	1.0	3:24
	SF	35					54	"	"	6:00
	SF	35	FA-N	79			52	"	"	6:00
	SF	35	PERL	8.5	BENT	2	116	"	"	6:00
	SF	35	NaCl	37*			54	"	"	6:00
	SF	35	NaCl	10*			54	"	"	6:47
	SF	35	KCl	37*			54	"	"	7:42
	SF	35	KCl	10*			54	"	"	3:14
	SF	35	LP7	50			108	"	"	0:36
	SF	35	DE	8.9			91	"	"	6:00
	SF	35	COAL	27			63	"	"	5:00
	SF	35	ILLM	27			63	"	"	5:00
	SF	35	SSS	2.5			122	"	"	6:00
	SF	35	SSM	4.4			130	"	"	0:38
	SF	20	DE	20			125	"	"	7:00
	SF	35	NaCl	5*	BENT	16	135	"	"	7:00
Unadeep "J"	None						44	1	0.2	0:36
	None						44	"	0.4	6:00
	DE	8.86					81	"	0.2	0:54
	DE	8.86					81	"	0.4	0:50
	DE	8.86					81	"	0.6	0:36
	FA-N	79					75	"	0.2	1:05
	FA-N	79					75	"	0.4	6:00
	LP7	50					98	"	0.2	0:43
	LP7	50					98	"	0.4	0:42
	LP7	50					98	"	0.6	0:26
	PERL	8.5	BENT	2			106	"	0.2	3:18
	BENT	4					65	"	0.2	1:12
	BENT	4					65	"	0.4	4:03
	BENT	8					86	"	0.2	1:47
	BENT	8					86	"	0.4	2:02
	NaCl	37*					44	"	0.2	4:52
	KCl	10*					44	"	0.2	6:00
	SSS	2					90	"	0.2	6:00
Fondu	FA-N	85					81	1/2	1.5/1.5	6:00
	FA-N	85					81	2	1.5	0:30
	FA-N	85					81	3	4.0	0:15
Slag Cement	SF	35					56	1	0.75	1:06
	SF	35	PP	10			75	4	4.0	0:20

Table II. (Cont)

<u>Cement</u>	<u>Code</u>	<u>Additives (Percent BWOC)</u>				<u>Amt.</u>	<u>% Water</u>	<u>Retarder</u>		<u>Thick Time</u>
		<u>Amt.</u>	<u>Code</u>	<u>Amt.</u>	<u>Code</u>			<u>Code</u>	<u>Amt. (%)</u>	
Silica:Lime, 1:1	None						96	1	0.5	2:08
	PERL	8.5	BENT	2			110	"	0.5	1:43
	FA-N	79					130	"	0.5	0:44
	FA-N	79					130	"	1.0	2:06
Milwhite Pozz:Lime, 1:0.42	None						142	"	0.5	0:58
Ideal "B"	SAND	35					56	1	0.3	0:57
	SAND	35					56	"	0.6	1:14
	SF	35					56	"	0.3	1:22
	SF	35					56	"	0.6	0:55
	SF	35	FA-L	79			54	"	0.3	0:42
	SF	35	PERL	8.5	BENT	2	118	"	0.3	0:59
	SF	35	PERL	8.5	BENT	2	118	"	0.6	6:00
	SF	35	NaCl	37*			56	"	0.6	0:37
	SF	35	KCl	37*			56	"	0.6	0:27
	SF	35	LP7	50			110	"	0.6	0:39

* Note: Percent by weight of water in these cases.

Retarder Codes:CodeMaterial

1

Proprietary blend of sugar and lignin derivatives.

2

Organic acid.

3

Proprietary blend of lignin and inorganic salts.

4

Metallic oxide.

Additive Codes:CodeMaterial

BENT

Bentonite

COAL

Powdered Coal

DE

Diatomaceous Earth

FA-L

Fly Ash - LaDue

FA-N

Fly Ash - Needles

ILLM

Illmenite

PERL

Perlite

LP7

Aerox Pozzolan

PP

Plaster of Paris

SF

Silica Flour

SAND

Silica Sand - 100 mesh

SSM

Sodium Silicate - Modified

SSS

Sodium Silicate - Solid

Table III. API liner cementing schedule 30M (from API Bulletin RP-10B).
 Conditions: Surface pressure = 2000 psi, Time to reach
 bottom = 34 min., Temperature gradient = 3.4°F/100 ft.,
 Total simulated depth = 8000 ft.

<u>Time (minutes)</u>	<u>Pressure (psi)</u>	<u>Deg. F</u>	<u>Deg. C</u>
0	2000	80	27
2	2800	93	34
4	3700	106	41
6	4500	119	48
8	5300	132	56
10	"	145	63
12	"	158	70
14	"	171	77
16	"	184	84
18	"	198	92
20	"	211	99
22	"	224	107
24	"	237	114
26	"	250	121
28	"	263	128
30	"	276	136
32	"	289	143
34	"	300	149
Bottom-Hole Static Temperature:		352	178

Table IV. Thickening time tests for furfuryl alcohol/coal system.
 See Table III for temperature/pressure programming.

<u>Run</u>	<u>System</u>	<u>Thickening Time (Hrs.: Min.)</u>	<u>Slurry Condition</u>
1	Furfuryl Alcohol ("neat")	6:00	Poured out
2	"	3:58	Poured out
3	48.8 % Furfuryl Alcohol, 48.8 % Powdered Coal, 2.4 % Malic Acid Soln. (50%)	0:31	Set

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Appendix 5

HIGH TEMPERATURE CEMENTING MATERIALS
FOR COMPLETION OF GEOTHERMAL WELLS

Quarterly Technical Progress Report
December 1977 - February 1978

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Date Published - April 12, 1978

PREPARED FOR THE UNITED STATES DEPARTMENT
OF ENERGY/BROOKHAVEN NATIONAL LABORATORY

Under Contract No. 420825-S

NOMENCLATURE

I	- Type I Portland Cement
III	- Type III Portland Cement
V	- Type V Portland Cement
G	- Class G Oil Well Cement
H	- Class H Oil Well Cement
J	- Class J Oil Well Cement
SF	- Silica Flour
HL	- Hydrated Lime
BFS	- Blast Furnace Slag
AP	- Aluminum Phosphate
PT	- Perlite
P	- Pozzolan
CMC	- Carboxy Methyl Cellulose
CMHEC	- Carboxy Methyl Hydroxy Ethyl Cellulose
COT	- Cream of Tartar
CAL	- Calgon
BOR	- Boric Acid
t_T	- Thickening Time
t_s	- Setting Time
W?C	- Water to Solids Ratio

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HIGH TEMPERATURE CEMENTING MATERIALS FOR COMPLETION OF GEOTHERMAL WELLS

Quarterly Technical Progress Report
December - February, 1978

INTRODUCTION AND SUMMARY

Execution of the project on the development of cementing materials for completion of geothermal wells was continued at planned level of effort as a part of the overall geothermal energy development program by the Geothermal Energy Division of the U.S. Department of Energy. High temperature cementing materials development projects which are monitored by the Brookhaven National Laboratory for the GTE Division of DOE is a small but very integral part of the overall geothermal energy development program efforts which encompass areas such as exploration of geothermal resources, classification and sizing of geothermal reservoirs, measurement of geothermal fluid properties, disposal of geothermal effluents, and corrosion and scale deposition in geothermal installations.

Phases I and II of the four-phase program have not been completed. During Phase II, more than 700 blends were evaluated at room temperature in terms of their initial viscosities, thickening and setting time. Some of the compositions were determined to have thickening times of two weeks or longer. Those cementing blends with long thickening and setting times were subjected to autoclave curing, and setting behavior under high temperature and pressure conditions were evaluated. The analysis of the results and discussion follow.

PROGRAM SCHEDULE

The first two phases of the program have been completed within or slightly ahead of schedule and ground work has been completed for Phase III and Phase IV studies. Limited use will be made of Dowell's facilities in the execution of Phase III studies which consist of measurement of thickening times with high temperature and pressure consistometer. High temperature and pressure vessels to be employed in the long-term curing of the cementing compositions for

preparation of mechanical and stability tests have been assembled and the instron mechanical testing machine has been equipped with the high temperature and pressure cell for mechanical strength measurements.

CURRENT PROGRESS

The laboratory research program is comprised of four main work phases.

Phase I: Define the current state of knowledge regarding the cementing of geothermal wells - procedures and materials.

Phase II: Select cements for the laboratory evaluation and develop and use screening procedures for identifying the most promising materials.

Phase III: Evaluate cements selected on the basis of their performance in Phase II relative to performance criteria established by BNL/DOE.

Phase IV: Prepare detailed final report of research procedures and findings and develop plans for further studies of potentially useful cements developed in the program.

The approach will use and build upon existing knowledge in developing cementing materials with improved performance for the application of interest. For this period, the work was involved with Phase I and Phase II as follows.

Phase I: Define the Current State of Knowledge Regarding the Cementing of Geothermal Wells - Procedures and Materials

The objective of this work phase is to identify, analyze, and document the experiences and research findings relating to the use of cementing materials for the completion of geothermal wells. The information and data of interest from the open literature and through telephone and personal interviews with knowledgeable individuals from oil and cement industries have been summarized.

Phase II: Select Cements, Additives, and Admixtures for the
Laboratory Evaluation and Development and Use of Screening
Procedures for Identifying the Most Promising Materials

Based on our understanding of the research problem and guided by the results of the Phase I work, a number of cements, modifiers, and admixtures have been selected for evaluation. A large number of cementing compositions - literally hundreds of batches - have been formulated and screened on the basis of their rheological behavior and thickening and setting times.

Phase II Studies - Initial Screening Tests

Room temperature and atmospheric pressure evaluation of the thickening and setting behavior of various cementing compositions was continued, employing the experimental procedures described previously.* Approximately 700 to 800 compositions have been screened in this phase of studies.

Tables 1 through 8 summarize the preliminary screening data on the thickening and setting behavior of the compositions thus far evaluated.

In Table 1, hydration behavior of Type I portland cement in the presence of various additives is summarized. As expected, Type I portland cement, even in the presence of large amounts of additives, sets too fast to be suitable for geothermal cementing applications. The same analysis holds for Types III and V portland cements, the evaluation data of which are presented in Tables 2 and 3, respectively. These results were not entirely unexpected, of course. A partial reason for evaluating these amounts was for the sake of completeness.

Tables 4 through 8 present the initial screening data on cementing compositions formulated with Class G, Class H, and Class J oil well cements constituting the hydraulic components in the batches.

Chemical analyses and some of the relevant physical test data are given for Class G and Class H oil well cements in Tables 10 and 11, respectively.

As Tables 4 through 8 indicate, oil well cements blended with various additives exhibit much longer thickening and setting times than portland cements. The two parameters (thickening and setting times) increase from Class G to Class J cements and with increasing additive contents.

* First Quarterly Technical Progress Report for September 1 - November 30, 1977.

Autoclave Evaluations

A number of cement-additive blends were subjected to autoclave curing at 450 F and saturated steam pressure at 450 F for a prescribed length of time. The cement slurries for this were prepared in the same manner as in Phase II studies. The slurries then were placed in sealed glass ampoules and subjected to autoclave curing with heating rates of 40 F/minute until 240 F and 1-4 F/minute thereafter. Ultimate temperature (400 to 450 F) is reached within 3 to 3.5 hours.

These experiments were carried out to determine a ballpark figure for the thickening times of various slurries before more precise thickening time measurements could be made. In these experiments the slurries will generally exhibit lower thickening and setting times than when measured with the high temperature and pressure consistometer, because the former case illustrates a static state while the latter determines the time parameters under dynamic conditions. Approximately 60 different compositions were evaluated under autoclave conditions.

A number of ampoules were broken during the cooling of autoclave as efforts were made to get the samples out as quickly as possible. Fast cooling rate of the autoclave chamber causes significant pressure gradients between the autoclave chamber and sealed glass ampoules resulting in breakage of the ampoules. Sufficient number of samples, however, were evaluated to enable us to obtain some data on setting behavior of these cements at 450 F and saturated steam pressure at 480 F.

Thickening Time Measurements at Elevated Temperatures and Pressures

Thickening time measurements were made on two cementing compositions using the high temperature and pressure viscometer which was developed at Battelle. A sketch and description of the apparatus is given on the following pages. Using this apparatus proved to be very cumbersome and laborious. Because of the intricacies involved in the apparatus, it was impossible to get the cement slurry in the autoclave out fast enough (once the thickening time was reached) before the cement set. This necessitated the replacement of expensive

containers after each measurement. Another problem which was encountered was that the up and down motion of the falling ball did not provide sufficient agitation (stirring action) to keep the cement slurry uniform in the autoclave, leading to erroneous readings.

High Temperature and Pressure Viscometer

This viscosity apparatus, which was tried at elevated temperature and pressure conditions, was developed by Battelle's research and development staff to study the viscosity changes of synthoil liquids which are the products of coal liquefaction processes. Figures 1 and 2 are a schematic diagram and a photograph of the apparatus, respectively. The principle of operation of the instrument is based on the falling ball method.

An autoclave (1) constitutes the outer cylinder, and a spherical bob (2) forms the falling ball. It is attached by tubing (3), through an insulating connector (4) to an Alnico V bar magnet (5). The magnet moves freely inside a tube extending from the top of the autoclave. Small glass spacers, fixed at the top of the bob, help keep the magnet centered in the autoclave. Outside the pressure system are two coils (6), part of the stirring mechanism provided with the autoclave. When a constant current is applied to one of these coils, an upward or downward force is exerted on the bob depending on the direction of the current flow. As the magnet passes through the second coil, a flow of current is induced, whereby the direction and rate of motion of the bob are detected. A vibrator helps to keep the bob moving smoothly.

The autoclave is provided with a furnace (7). Without modification the contents of the autoclave are subject to severe temperature gradients, since heat is lost rapidly from the head as well as from the bottom. To improve the temperature control, an auxiliary furnace (8) is placed around the head. Thermocouples are inserted into the body of the autoclave near the top and near the bottom, and these are used to adjust the temperature of the autoclave and to equalize the temperatures at the top and bottom. A metal-sheathed thermocouple (9) is inserted through the head as shown so that it senses accurately the temperature of the medium near the bob. Ports for the introduction and withdrawal of gas, for pressure measurement and control, and for

Figure 1. Autoclave viscometer

Figure 2. Instrumented autoclave for measurement of viscosity, density and electrical properties

safety relief valve are provided, several entering through the head. Three of these are shown in Figure 1 (10). Pressures are controlled with a sensitive back-pressure regulator.

Procedure

The viscosity can be calculated from the force, F , acting on the bob and the velocity of the bob, v_b , based on Poiseuille flow in the annulus between the bob and the cylinder. The shear stress on the liquid at the surface of the bob is:

$$\sigma = \frac{F}{2\pi h R_b} \frac{(\beta^2 - 1)}{(\beta^2 + 1)}$$

and the shear rate is:

$$\dot{\gamma} = \frac{v_b}{R_b} \left[\frac{(\beta^2 + 1)}{(\beta^2 - 1)} \ln \beta - 1 \right]^{-1}$$

where h is the height of the bob,

R_b is the radius of the bob,

R_c is the radius of the cylinder, and

$$\beta = R_c / R_b$$

The viscosity is:

$$\eta = \frac{\sigma}{\dot{\gamma}} = \frac{F}{2\pi h v_b} \left[\ln \beta - \frac{(\beta^2 - 1)}{(\beta^2 + 1)} \right]$$

The result is very sensitive to small errors in the measured radii. Therefore, the apparatus is calibrated using an oil of known viscosity.

The force, F , is related to the current passing through the activating coil in a series of measurements in which the magnet assembly with counterweights is suspended from the beam of an analytical balance. When the bob has traveled

approximately half way, the linear relationship between current and force is verified. This calibration is easily checked by finding the current necessary to balance the weight of the bob assembly in air.

Thickening Time Measurements with API Standard High Pressure Consistometer

Preliminary thickening times on a few compositions were also measured using the pressurized consistometer used in API thickening time tests. A modified version of Schedule 32 was employed in the test procedure. Final temperature was 420 F.

The slurries were prepared according to API specifications at water-to-cement ratios of 0.5 with 0.5 percent admixture levels by weight of solids. Heating rate was maintained at 7.5 F. Final temperature of 450 F was obtained in 50 minutes, and temperature was maintained at 450 F until a cement slurry consistency of 100 units of consistency (U_c). The time at which the viscosity of the cement slurry reaches 100 U_c is defined as the thickening time. Thickening times measured as described above ranged between 2-1/2 to 5 hours for the samples evaluated.

FUTURE WORK

Preparations for Phase III and Phase IV studies are presently under way. Efforts will be devoted to completion of Phase III (thickening time determinations at high temperature and pressure) studies in the coming months. Also, those segments of the Phase IV studies that can be carried out concurrently with Phase III work will be given attention.

Table 1

Summary of Initial Screening Data on Blends With
Type I Portland Cement and Various Additives

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS		
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMEC	COT	CAL	BOR					
1	1.0	80											20										4	Couldn't measure
2	1.0	80						20																
3	0.6	80								20													5	
4	0.5	80							20														5	
5	0.6	80												20									4	
6	1.0	70											30											
7	1.0	70						30														4		
8	0.65	70								30												4		
9	0.5	70							30													5		
10		70												30								4		
11	1.0	80						40														2	Set too fast " " " " " " " "	
12	0.65	60								40														
13	0.5	60								40														
14	0.5	60												40										
15	1.0	70						30										0.5						
16	1.0	70											30					0.5						
17	0.65	70							30									0.5						
18	0.6	70								30								0.5						
19	0.5	70									30							0.5						
20	0.5	70												30				0.5						
21	1.0	70						30							0.5									
22	1.125	70											30		0.5									
23	0.65	70							30						0.5									
24	1.0	70								30					0.5									

Table 1 (Continued)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL	BOR			
25	0.5	70									30				0.5							Set too fast
26	0.6	70												30	0.5							"
27	1.0	70						30														"
28	1.0	70											30				0.5					"
29	0.65	70							30								0.5					"
30	1.0	70								30							0.5					"
31	0.5	70															0.5					"
32	0.5	70															0.5					"

Table 2

Summary of Initial Screening Data on Blends With
Type III Portland Cement and Various Additives

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)						ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS		
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL				BOR	
1	0.55	70	100																		3	24 hr. Meas. Visc. "7 hr. soft 4-1/2 hr. soft	
2	0.9		70					30															5-1/2
3	0.9		70										30										5-1/2
4	0.5		70						30														5-1/2
5	0.6		70							30													3
6	0.5		70								30												5-1/2
7	0.55		70										30										5-1/2
8	1.15		70					30										0.5					7
9	0.9		70										30					0.5					24
10	0.5		70						30									0.5					30-1/2
11	0.7		70							30								0.5					24
12	0.5		70								30							0.5					30
13	0.5		70											30				0.5					30
14	1.05		70					30									0.5						
15	1.0		70										30				0.5						4
16	0.5		70						30								0.5						2
17	0.6		70							30							0.5						1
18	0.5		70								30						0.5						1
19	0.5		70											30			0.5						1/2
20	1.1		70					30							0.5								24
21	0.9		70										30		0.5								24
22	0.5		70												0.5								24
23	0.7		70							30					0.5								24
24	0.5		70												0.5								24
25	0.55		70											30	0.5								24

Table 3

Summary of Initial Screening Data on Blends With
Type V Portland Cement and Various Additives

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)						t _T (hours)	t _S (hours)	OBSERVATIONS	
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMHEC	COT	CAL	BOR					
1	0.5			100																				7 hr. soft
2	1.5			70				30																
3	1.0			70									30											
4	0.5			70					30															
5	0.55			70						30														
6	0.5			70							30											6		6 hr. soft
7	0.5			70										30								7		6 hr. soft
8	1.3			70				30										0.5						6 hr. soft
9	1.0			70									30					0.5						30 hr. meas. visc.
10	0.5			70					30									0.5						"
11	0.6			70						30								0.5				6		
12	0.5			70							30							0.5						
13	0.55			70										30				0.5						
14	1.0			70				30							0.5									
15	1.3			70									30		0.5									
16	0.5			70					30						0.5									
17	0.8			70						30					0.5									
18	0.6			70							30				0.5									
19	0.7			70										30	0.5									
20	2.1			70				30									0.5							5 hr. soft
21	1.0			70				30					30				0.5					5		
22	0.5			70					30								0.5							
23	0.5			70						30							0.5					5		
24	0.5			70							30						0.5					5		
25	0.5			70									30				0.5					5		

Table 4

Summary of Initial Screening Data on Blends With
Class G Oil Well Cement and Various Additives

SEQ No	W/C	CEMENTS (WtX)						ADDITIVES (WtX)							ADMIXTURES (WtX)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SP	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL	BOR			
1	1.0				70			30														
2	1.15				70								30									
3	0.5				70				30													
4	0.6				70					30												
5	0.6				70						30											
6	0.5				70									30								
7	0.5				100																19	
8	1.05				70			30							0.5							25 hr. soft
9	1.0				70								30		0.5							
10	0.5				70				30						0.5							
11	0.75				70					30					0.5							
12	0.5				70						30				0.5							
13	0.55				70									30	0.5							
14	1.5				70			30										0.5				
15	1.0				70								30					0.5				
16	0.5				70				30									0.5				
17	0.55				70					30								0.5			6	
18	0.5				70						30							0.5				
19	0.5				70									30				0.5			8	
20	1.5				70			30									0.5					18 hr. soft
21	1.0				70								30				0.5					
22	0.5				70				30								0.5					
23	0.5				70					30							0.5					18 hr. soft
24	0.5				70						30						0.5					
25	0.5				70									30			0.5					

Table 4 (Continued)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	MBEC	COT	CAL	BOR			
26	0.7				60							40								19	120	18 hr. soft " " " " Not set discarded 18 hr. soft " Not set " " " " " " " " " " " "
27	0.5				60				40												19	
28	0.5				60					40											19	
29	0.55				60								40								19	
30	0.7				60							40			0.5					1-1/2	120	
31	0.55				60				40						0.5					18	120	
32	0.5				60					40					0.5					18	24	
33	0.6				60								40		0.5					18	120	
34	0.55				100										0.5						96	
35	0.8				60							40				0.5				1	120	
36	0.55				60				40							0.5				18	168	
37	0.55				60					40						0.5				18	144	
38	0.65				60								40			0.5				18	120	
39	0.5				100											0.5				96	144	
40	0.7				60							40						0.5		96	168	
41	0.5				60				40									0.5			96	
42	0.5				60					40								0.5			96	
43	0.5				60								40					0.5		2	96	
44	0.5				100													0.5			96	
45	0.7				60							40					0.5			2	96	
46	0.5				60				40								0.5				96	
47	0.5				60					40							0.5				96	
48	0.55				60								40				0.5			4	96	
49	0.5				100												0.5			4	96	

Table 5

Summary of Initial Screening Data on Blends With Class G Oil
Well Cement and Various Additives (Two Additives Per Blend)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS			
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	MIEC	COT	CAL	BOR						
1	0.6					60			20		20				0.5								48		Hydrogen Sulfide Gas Noted Not Set
2	0.7					"			20			20			0.5							48	96		
3	0.7					"				20	20				0.5							48	96		
4	0.5					"			20							0.5						5	118		
5	0.7					"			20			20				0.5						24	96		
6	0.7					"				20	20					0.5							24		
7	0.5					"			20		20											6	24	Hydrogen Sulfide Gas No <	

Table 6

Summary of Initial Screening Data on Blends With
Class H Oil Well Cement and Various Additives

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL	BOR			
1	0.6				60				20		20				0.5					27	48	
2	0.7				60				20			20			0.5						23	*
3	0.8				60						20	20			0.5					24	48	
4	0.5				60				20		20									5	22	
5	0.6				60				20			20								3	22	
6	0.7				60						20	20								3	22	*
7	0.5				60				30		10									45 min	17	
8	0.5				60				30			10								20 min	17	
9	0.5				60						30	10								20 min	17	*
10	0.5				60				10		30									7	24	
11	0.7								10			30								24	120	
12	0.7				60						10									24	120	*
13	0.5				60				20		20					0.5				27	168	
14	0.7				60				20			20				0.5					22	
15	0.7				60						20	20				0.5					22	
16	0.55				60				30		10				0.5					24	48	
17	0.6				60				30			10			0.5					5	23	
18	0.7				60						30	10			0.5					2	4	
19	0.6				60				10		30				0.5					24	48	
20	0.7				60				10			30			0.5					27	120	
21	0.5				60				30		10					0.5				168	168	Not set
22	0.6				60						30	10				0.5				2	19	
23	0.5				60				10		30					0.5				120	144	
* Hydrogen sulfide gas given off.																						

Table 6 (Continued)

SEQ No	W/C	CEMENTS (WtX)						ADDITIVES (WtX)							ADMIXTURES (WtX)					t _T (hours)	t _S (hours)	OBSERVATIONS	
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL	BOR				
24	0.75				60				10			30				0.5					10	120	Not set "
25	0.5				60				30					10								72	
26	0.5				60						30			10								72	
27	0.5				"				10					30								"	
28	0.5				"						10			30								"	
29	0.5				"				20					20								"	
30	0.5				"						20			20								"	
31	0.6				"				30					10	1							"	
32	0.55				"						30			10	1							"	
33	0.6				"				10					30	1							"	
34	0.6				"						10			30	1							"	
35	0.6				"				20					20	1							"	
36	0.6				"						20			20	1							"	
37	0.5				"				30					10		1				22	168		
38	0.55				"						30			10		1				22	"		
39	0.6				"				10					30		1				22	"		
40	0.6				"						10			30		1				48	"		
41	0.55				"				20					20		1				22	"		
42	0.55				"						20			20		1				22	"		
43	0.5				50				50											5	21		
44	0.5				"						50									5	21		
45	0.55				"								50							5	21		
46	0.6				"				50						1						96		
47	0.6				"						50				1					21	27		

Table 6 (Continued)

SEQ No		CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS			
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMHEC	COT	CAL	BOR						
48	0.65				50									50	0.5									96	
49	0.55				"				50							0.5					21	168	Not set		
50	0.55				"						50					0.5							144		
51	0.55				"									50		0.5				28	144				
52	0.5				"				20		30												72		
53	0.55				"				20					30									"		
54	0.55				"						20			30									"		
55	0.5				"				20		30												"		
56	0.5				60				20					20									"		
57	0.5				60						20			20									"		
58	0.6				50				20		30				0.5								"		
59	0.6				"				20					30	0.5								"		
60	0.6				"						20			30	0.5								"		
61	0.6				"				30		20				0.5								"		
62	0.6				"				30					20	0.5								"		
63	0.6				"						30			20	0.5								"		
64	0.55				"				20		30					0.5				72	168	Not set			
65	0.6				"				20					30	0.5					"	"				
66	0.6				"						20			30	0.5					"	120				
67	0.55				"				30		20				0.5					"	168	Not set			
68	0.6				"				30					20	0.5					"	"	"			
69	0.6				"						30			20	0.5					"	96	Not set			

Table 7

Summary Blends With Class H Oil Well Cement and
Various Additives (Two Additives Per Blend)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL	BOR			
1	0.5					100															24	
2	1.0					70		30												6	0	
3	0.8					"							30								24	6 Hour Soft
4	0.5					"			30												24	
5	0.55					"				30											6	
6	0.5					"					30										24	
7	0.5					"								30							24	6 Hour Soft
8	2.0					"		30										0.5			24	
9	1.0					"							30					0.5				24 Hour Meas. Visc.
10	0.5					"			30									0.5				" " " "
11	0.5					"				30								0.5				" " " "
12	0.5					"					30							0.5				72 Hour Meas. Visc.
13	0.5					"								30				0.5				7 Hour Soft
14	2.0					"		30										0.5			24	
15	1.0					"							30					0.5			72	
16	0.5					"			30									0.5				168 Hour Meas. Visc.
17	0.5					"				30								0.5				" " " "
18	0.5					"					30							0.5				" " " "
19	0.5					"								30				0.5			144	
20	1.1					"									0.5						24	6 Hour Soft
21	0.9					"									0.5						144	
22	0.5					"									0.5						48	
23	0.6					"									0.5						24	6 Hour Soft
24	0.5					"									0.5					10.25	4	

Table 7 (Continued)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMHC	COT	CAL	BOR			
25	0.55					70									0.5							
26	0.7					50						40								10.25	4	
27	0.5					60			40											5	22	
28	0.5					60					40										22	4 Hour Soft
29	0.55					60								40						7	22	" " "
30	0.7					60						40			0.5					1-1/2	24	19 Hour Meas. Visc.
31	0.5					60			40						0.5					36	48	" " " "
32	0.55					60					40				0.5					36	48	" " " "
33	0.6					60								40	0.5					36	48	" " " "
34	0.5					100									0.5					36	48	" " " "
35	0.75					60						40				0.5				20 min.	4	
36	0.5					60			40							0.5				22	168	Not Set
37	0.5					60					40					0.5				22	168	4 Hour Meas. Visc.
38	0.55					60								40		0.5				22	168	" " " "
39	0.5					100										0.5				22	168	" " " "
40	0.7					60						40						0.5		0.5	4	21 Hour Meas. Visc.
41	0.5					60			40									0.5		24	48	" " " "
42	0.5					60					40							0.5		36	48	" " " "
43	0.5					60								40				0.5		21	48	21 Hour Soft
44	0.5					100												0.5		36	48	21 Hour Meas. Visc.
45	0.7					60						40					0.5			0.25	2	
46	0.5					60			40								0.5				168	Not Set Meas. Visc.
47	0.5					60					40						0.5			144	168	Not Set
48	0.5					60								40			0.5			24	48	18 Hour Meas. Visc.
49	0.5					100											0.5				168	Not Set Meas. Visc.

Table 8

Summary of Initial Screening Data on Blends With Class J Oil
Well Cement and Various Additives (Two Additives Per Blend)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL	BOR			
1	0.6						60		20		20				0.5					48	168	
2	0.7						"		20			20			0.5					72	168	Not Set
3	0.75						"				20	20			0.5						168	" "
4	0.5						"		20		20					0.5				96	168	" "
5	0.75						"		20			20				0.5				96	168	" "
6	0.7						"				20	20				0.5				96	168	" "
7	0.5						"		20		20									22	144	" "
8	0.65						"		20			20								144	168	" "
9	0.7						"				20	20								144	168	" "
10	0.5						"		30		10									28	96	
11	0.6						"		30			10									168	Not Set
12	0.6						"		10		30									21	96	
13	0.75						"		10			30								120	144	
14	0.5						"		30		10				0.5					144	168	Not Set
15	0.6						"		30			10			0.5					144	168	" "
16	0.55						"		10		30				0.5					96	20	
17	0.7						"		10			30			0.5					18	96	
18	0.5						"		30		10					0.5				120	168	Not Set
19	0.65						"		30			10				0.5					168	" "
20	0.5						"		10		30					0.5				144	168	" "
21	0.65						"		10			30				0.5				96	120	
22	0.5						"		30					10						28	144	
23	0.5						"				30			10						24	48	
24	0.5						"		10					30						24	48	
25	0.5						"				10			30						24	48	

Table 8 (Continued)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS	
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL	BOR				
26	0.5						60		20					20							24	48	Not Set
27	0.5						"				20			20							24	48	
28	0.5						"		30					10	0.5						144	168	
29	0.55						"				30			10	0.5						48	120	Not Set
30	0.55						"		10					30	0.5							168	
31	0.55						"				10			30	0.5						120	168	
32	0.5						"		20					20	0.5						120	168	Not Set
33	0.55						"				20			20	0.5						48	120	
34	0.55						"		30					10		0.5					144	168	
35	0.55						"				30			10		0.5					144	168	" "
36	0.6						"		10					30		0.5					144	168	" "
37	0.6						"				10			30		0.5					144	168	" "
38	0.6						"		20					20		0.5					168	168	" "
39	0.6						"				20			20		0.5					144	168	" "
40	0.5						50		50												72	96	Not Set but visc
41	0.5						"				50											72	
42	0.5						"							50								72	
43	0.5						"		50							0.5						168	Not Set
44	0.55						"				50					0.5					72	96	
45	0.55						"							50		0.5						168	
46	0.5						"		50								0.5					168	" "
47	0.55						"				50						0.5					168	" "
48	0.55						"							50			0.5					168	" "
49	0.5						"		20		30											72	

Table 8 (Continued)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL	BOR			
50	0.5						50		20					30						>20	72	
51	0.5						"				20			30						>20	72	
52	0.5						"		30		20									>20	72	
53	0.5						"		30					20						19	72	
54	0.5						"				30			20						19	72	
55	0.5						"		20		30				0.5					72	168	
56	0.55						"		20					30	0.5						168	Not Set
57	0.6						"				20			30	0.5					72	168	
58	0.6						"		30		20				0.5					96	168	
59	0.55						"		30					20	0.5						168	Not Set
60	0.6						"				30			20	0.5					72	168	
61	0.55						"		20		30					0.5					168	Not Set or Thickened
62	0.6						"		20					30		0.5					168	
63	0.6						"				20			30		0.5					168	" " "
64	0.6						"		30		20					0.5					168	" " "
65	0.6						"		30					20		0.5					168	" " "
66	0.6						"				30			20		0.5					168	" " "

Table 9

Cement Composition With Thickening
Times Longer Than 24 Hours

SEQ No		CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	CMIEC	COT	CAL	BOR			
1	0.5						70		30						0.5					48	168	Not set
2	0.55						70				30				0.5					48	168	
3	0.55						70							30	0.5					168	168	Not set
4	0.5						100								0.5					144	"	"
5	0.5						70		30							0.5				48		
6	0.55						70				30					0.5				48		
7	0.55						70							30		0.5				48		
8	0.55						100									0.5					168	Not set
9	0.7						70					30						0.5		36	72	
10	0.5						70				30							0.5		48	168	Not set
11	0.5						70							30				0.5		48	120	
12	0.5						100											0.5		96	168	Not set
13	0.55						60				40				0.5					48	144	
14	0.6						60							40	0.5					48	168	Not set
15	0.55						60				40					0.5				144	"	"
16	0.6						60							40		0.5				144	"	"
17	0.5						60		40								0.5			120	"	"
18	0.5						60							40			0.5			120	"	"
19	0.7						60					40						0.5		96	"	"
20	0.5					60			40								0.5				"	"
21	0.5					60					40						0.5			144	"	"
22	0.7					60			20			20			0.5					48	96	
23	0.6						60		20		20				0.5					48	168	
24	0.7						60		20			20			0.5					72	168	Not set

Table 9 (Continued)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	MHEC	COT	CAL	BOR			
25	0.5						60		20		20					0.5				72	168	Not set
26	0.75						60		20			20				0.5				72	"	"
27	0.65						60		20			20								144	"	"
28	0.5				60				30		10					0.5				168	"	"
29	0.5				60				10		30					0.5				120	144	
30	0.55					60			30		10					0.5				120	168	Not set
31	0.5					60			10		30					0.5				96	168	
32	0.75						60		10			30								120	144	
33	0.5						60		30		10				0.5					144	168	Not set
34	0.6						60		30			10			0.5					144	"	"
35	0.55						60		10		30				0.5					96	120	
36	0.5						60		30		10					0.5				120	168	Not set
37	0.65						60		30			10				0.5					168	Not set or thick
38	0.5						60		10		30					0.5				144	168	Not set
39	0.65						60		10			30				0.5				86	120	
40	0.55						60		30					10	0.5					48	72	
41	0.6						60		10					30	0.5					48	72	
42	0.6					60					10			30	0.5					48	72	
43	0.55					60			20					20	0.5					48	72	
44	0.5						60		30					10	0.5					144	168	Not set
45	0.55						60				30			10	0.5					48	120	
46	0.55						60		10					30	0.5						168	Not set
47	0.55						60				10			30	0.5					120	"	
48	0.5						60		20					20	0.5					120	"	"

Table 9 (Continued)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	EMEC	COT	CAL	BOR			
49	0.55						60							20	0.5					48	120	
50	0.55						60		30					10		0.5				144	168	Not set
51	0.55						60				30			10		0.5				144	"	"
52	0.6						60		10					30		0.5				144	"	"
53	0.6						60				10			30		0.5				144	"	"
54	0.6						60		20					20		0.5				168	"	"
55	0.6						60				20			20		0.5				144	"	"
56	0.55				50						50					0.5				96	144	
57	0.5						50		50											72	96	
58	0.55						50				50				0.5					72	96	
59	0.55				50				20		30					0.5				72	168	Not set
60	0.6				50				20					30		0.5				72	168	
61	0.6				50						20			30		0.5				72	120	
62	0.55				50				30		20					0.5				72	168	Not set
63	0.6				50				30					20		0.5				72	168	"
64	0.6				50						30			20		0.5				72	96	
65	0.6					50			20					30	0.5					48	72	
66	0.6					50			30					20	0.5					48	72	
67	0.55					50			20		30					0.5				96	168	Not set
68	0.6					50					20			30		0.5				96	168	
69	0.5					50			30		20					0.5				96	168	
70	0.6					50			30					20		0.5				168	168	Not set
71	0.6					50					30			20		0.5				96	168	
72	0.5						50		20		30				0.5					72	168	

Table 9 (Continued)

SEQ No	W/C	CEMENTS (Wt%)						ADDITIVES (Wt%)							ADMIXTURES (Wt%)					t _T (hours)	t _S (hours)	OBSERVATIONS
		I	III	V	G	H	J	B	SF	HL	BFS	AP	PT	P	CMC	PMHEC	COT	CAL	BOR			
73	0.55						50		20					30	0.5						168	Not set or thick
74	0.6						50				20			30	0.5					72	168	
75	0.6						50		30		20				0.5					96	168	
76	0.6						50				30			20	0.5					72	168	

TABLE 10. CHEMICAL ANALYSIS AND PHYSICAL TESTS ON CLASS G CEMENT

<u>Chemical Analysis Data</u>	
SiO ₂	21.9
Al ₂ O ₃	3.6
Fe ₂ O ₃	3.4
CaO	63.4
MgO	4.5
SO ₃	2.1
Loss	1.3
Na ₂ O	0.15
K ₂ O	0.44
Eq. Na ₂ O	0.44
C ₄ AF	10
C ₃ A	4
C ₂ S	20
C ₃ S	56
<u>Physical Test Data</u>	
Blaine Fineness	3020
Wagner Fineness	1600
API Schedule 5	
Thickening Time	104 minutes
Viscosity	13 Bc
Free Water	2.9 ml.
Compressive Strength	
Schedule 1-S	510 psi

TABLE 11. CHEMICAL ANALYSIS & PHYSICAL TESTS ON CLASS H CEMENT

<u>Chemical Analysis Data</u>	
SiO ₂	23.3
Al ₂ O ₃	3.6
Fe ₂ O ₃	3.3
CaO	65.2
MgO	1.4
SO ₃	2.6
Loss	0.7
Insol.	0.1
K ₂ O	0.2
Na ₂ O	0.3
Total as Na ₂ O	0.4
C ₃ S	52
C ₃ A	4.0
<u>Physical Test Data</u>	
Wagner	1600
Blaine	2600
-325	82.6
Normal Consistency	22.0
Vicat	3:30
Autoclave Exp.	0.1
C-109 Cubes	
1-day	660
3-days	1930
API Cubes	
1-S	670
3-S	2070
Thickening Time API Schedule 5	120 min.

Appendix 6

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

A report to
Brookhaven National Laboratory
Upton, Long Island, New York 11973

for
Contract No. 422272-S

Principal Investigator:
Della M. Roy
Professor of Materials Science

March 1, 1978

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

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I. INTRODUCTION

This report summarizes new results obtained during the second quarter of the project. The synthesis and reactions of cementitious materials continues along lines established last quarter. The property measurement apparatus for viscosity, permeability, microhardness and compressive strength is now generally functional and the first measurements are reported.

II. EXPERIMENTS IN THE $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ SYSTEM

A. Stock Chemical and Gel Starting Materials

Initial investigation and observation of the experiments carried out to date indicate that under the hydrothermal conditions being investigated (400°C , 10,000 psi, 68.9 MPa) the most promising composition regions for geothermal cements with the desired properties are those which occur in the more SiO_2 and CaO-rich portions of the system. Compositions containing quantities of MgO in excess of 30 weight percent appear to be of little value as a cementing material. This observation is in agreement with data available (Speakman and Majumdar, 1971) on cement compositions containing high levels of MgO, e.g. those formulated from dolomitic limestones where the deterioration and poor quality of cements is attributed to the formation of brucite, $\text{Mg}(\text{OH})_2$.

Asbestos-containing cements have been developed and are known to be particularly suitable for hydrothermal applications. The asbestos fiber may be a serpentine (chrysotile) or amphibole (tremolite, anthophyllite) and so such cement products correspond to compositions in the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ system.

At present, phase equilibrium studies in the pure and cementitious formulations are being restricted to compositions containing >35 weight percent SiO_2 marked by the solid line in Figure 1.

Four hydrated phases have been encountered within the composition region being investigated. These are the calcium-silicate hydrates:

xonotlite, $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ and gyrolite, $\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. The magnesium silicate hydrates identified are chrysotile, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. No ternary calcium magnesium silicate hydrate species have been identified.

Of the four hydrated phases encountered only xonotlite, chrysotile, and talc have been synthesized in pure form. Attempts to obtain a pure gyrolite preparation under identical hydrothermal conditions have not succeeded. Instead, although gyrolite can be detected as a major product of reaction in experiments of up to approximately seven days duration it is always encountered in association with substantial quantities of xonotlite and quartz. In hydrothermal runs of longer duration, e.g. 14-21 days, gyrolite dissociates completely to xonotlite + SiO_2 .

These observations on calcium silicate formation are reflected in phase equilibria in the ternary compositions for binary and ternary compositions close to that of gyrolite (e.g. 5, 6, 8 and 9 in Fig. 1). Gyrolite is observed in hydrothermal experiments of short duration, typically several days and is not a stable phase product in more prolonged runs. The formation of gyrolite in high- SiO_2 environments from calcium silicate hydrate phases stable at lower temperatures and pressures, e.g. tobermorite, $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$, has been reported (Roy and Harker, 1962) but much lower temperature and pressure conditions than those at present being investigated.

Tobermorite, a common binding phase in autoclaved calcium silicate hydrothermal well cements is known to convert at 150 - 200°C to xonotlite and gyrolite (Roy and Harker, 1962). Above this temperature range xonotlite and truscottite are reported as the stable phases. The latter phases have not been encountered in the present study but experiments on the join $\text{CaO-SiO}_2 + \text{H}_2\text{O}$ at 10,000 psi and 400°C are continuing. It is assumed that gyrolite is not a stable phase under the present hydrothermal conditions but may well become so at lower temperatures and pressures.

In Table 1, details of the phases observed for the various compositions investigated are given; the numbered compositions correspond to those in Figure 1.

Figure 1. Numbered compositions correspond to those being investigated in the CaO-MgO-SiO₂ system.

TABLE 1

Phases Observed for the Compositions after Reaction at 400°C, 10,000 psi.

Composition Number	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 (talc)	7	talc + MgO + quartz
	21	talc
13 (chrysotile)	3	chrysotile (poor crystallinity)
	21	chrysotile
14 (xonotlite)	3	xonotlite + gyrolite + quartz
	21	xonotlite
15 (gyrolite)	7	gyrolite + xonotlite + quartz
	21	xonotlite + quartz
16	7	xonotlite + monticellite (trace)
	17	xonotlite + monticellite
17	21	chrysotile + monticellite (trace)

B. Unadeep Cement + Oxides as Starting Materials

In order to minimize time consumption and to optimize conditions for the interpretation of experimental results for the studies in the "pure" and cement systems, two parallel experiments are carried out for each composition studied. These are:

i) A study of phase equilibria in the "pure" system utilizing either amorphous gels or the pure stock chemicals: $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, and SiO_2 (quartz) as starting materials.

ii) Phase equilibria studies on identified compositions using the appropriate quantities of commercially available cement Unadeep + MgO + "Minusil" (5μ quartz) as starting materials.

In experiments carried out as in (ii), i.e. with commercially available Unadeep cement + MgO + SiO_2 as required, gyrolite has not been encountered in any compositions. With compositions in the triangle xonotlite-talc- SiO_2 , only these three phases have been encountered. The ternary calcium magnesium silicate, tremolite, $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ has not been observed although evidence from the mineralogical literature (Slaughter, Kerrick and Wall, 1975) suggests that this phase may be stable within the present temperature and pressure range being investigated.

Both experiments are performed under identical conditions of time, temperature, and pressure in open or sealed 2-1/2 cm x 5 mm i.d. gold tubes. Both samples are then examined by x-ray diffractometry and petrographic microscope to determine phase assemblages. The small samples obtained in (ii) are also of sufficient size to permit an initial microhardness determination. Although this is not intended as a definitive strength test of a particular sample, it can be used to estimate the potential of a particular composition or range of compositions for further, more extensive study.

Hydrothermal runs of variable duration are made for each sample; this permits the observation and identification of any intermediate compounds formed in the development of the stable phase assemblages.

In Fig. 1, the compositions for which phase equilibria have been or are being determined are indicated and numbered individually.

For the compositions prepared with Unadeep + oxide/hydroxide mixtures which appear to indicate potentially useful cementing properties, a number of larger samples are prepared for individual hydrothermal treatment in larger autoclaves. At present, composition #6 has been selected for further study and larger samples measuring approximately 1 x 2-1/2 inches had been prepared by autoclaving at 400°C and 10,000 psi for 23 days and a report on the results for the microhardness and compressive strength are given in this report.

In addition to the hydrated silicate species identified in compositions containing approximately equal quantities of those component oxides, i.e. those lying within the shaded area of Fig. 1, a major product of hydrothermal treatment appears to be a phase closely resembling the anhydrous compound monticellite CaO-MgO-SiO_2 . This phase has been encountered in association with hydrated phases, e.g. xonotlite and chrysotile but only in samples prepared from stock chemicals and gels. This region of the phase diagram has not yet been studied in detail with Unadeep cement preparations. Other studies in phase equilibria relevant to this system (Petrovic, 1973) in the temperature range 25 - 350°C indicate compatibility of a serpentine phase (chrysotile) with calcium silicate hydrate species. On the other hand alternative data (Roy, 1956) suggests that monticellite is stable instead and its hydrothermal synthesis has been reported as low as 475°C.

The phase equilibria studies are continuing particularly on the join CaO-SiO_2 under the present hydrothermal conditions and also to determine the role of the anhydrous monticellite phase in the system. The details of phase relationships may become more evident in the studies now being investigated where a wider range of hydrothermal conditions will be studied.

III. EXPERIMENTS IN THE $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ SYSTEM

A. Stock Chemical and Gel Starting Materials

Hydrothermal studies in the system $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ are being conducted. The compositions of 15 mixtures prepared from oxides and gel starting materials are plotted on Fig. 2. Mixtures 1-9 have been reacted at 400°C and 10,000 psi (68.9 MPa) for varying lengths of time. Mixtures 10 - 15 and a sample of Unadeep cement are presently being reacted at 400°C and 10,000 psi. In addition mixtures 1 - 15 are presently being reacted at 300°C and 10,000 psi for 21 days. Shorter runs of 3 and 7 days are planned for mixtures 1 - 3 to determine the rate and metastable states of hydration.

Results of the completed runs indicates that mixtures 1, 3, 4, 6 and 8 are at least somewhat cementitious and mixtures 2, 5, 7 and 9 are not at 400°C and 10,000 psi,

Mixtures 1, 2 and 3 in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system shown in Fig. 2 have been hydrothermally treated at 10,000 psi and at 400 and 450°C. The samples were pelletized and run in an open system. Mixture 1 crystallized into wairakite + an unknown phase; mixture 2 crystallized as another compound which has not been identified; and mixture 3 crystallized into hydrogarnet, gehlenite hydrate, and boehmite.

A limit for cementitious compositions is also indicated on Fig. 2. The cementitious phase in runs 1, 4, 6 and 8 is wairakite. Phase identification of mixtures in the central portion of the diagram is still tentative and is probably the result of metastable anorthite hydrates. More work on phase identification is necessary for an understanding of the phase relations in this region.

Figure 3 is a summary of previous investigations in the system $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$. The 400°C and 4000 psi (27.6 MPa) isotherm is plotted here and was taken from Barrer and Denny (1961) and Koizumi and Roy (1960).

B. Secar Cement + Oxides as Starting Materials

Although the Secar cement appeared to be a very satisfactory starting material, some unexpected complexities were encountered in the Secar

Figure 2. Numbered compositions correspond to those being investigated in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system

Figure 3. Summary of previous investigations in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 400°C and approximately 4000 psi (27.6 MPa). (after Roy, 1956; Koizumi and Roy, 1960).

cement ($\text{CaO-Al}_2\text{O}_3$ [$+$ SiO_2]) starting material. An unexplained very intense peak at a d-spacing of approximately 2.93 Angstroms was found in the original XRD pattern. The peak disappears when the cement is heated to greater than 200°C . The x-ray diffraction pattern of the heated material is, as expected, a combination of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. No further work with this as a starting material is planned for the immediate future. Refcon cement, similar in composition, will be used instead.

Three new Refcon cement samples have been prepared and presently are being hydrothermally treated. Their compositions are listed in Table 2 and also in Fig. 2.

TABLE 2
Refcon-Cement Samples.

Sample No.	Cement Type	Composition				Water cement	Hydrothermal Treatment		
		Cement	Minusil	MgO	Perlite		Temp. ($^\circ\text{C}$)	Pressure (psi)	Time
HYD-3	Refcon	50g	74.34g		50g	0.800	450	1400	
HYD-4	Refcon	50g	8.04g		50g	0.800	450	1400	
HYD-5	Refcon	50g	35.67g		50g	0.800	450	1400	
*HYD-3		65.0%	SiO_2		22.5%	Al_2O_3		12.5%	CaO
*HYD-4		43.5%			36.5%			20.0%	
*HYD-5		55.0%			29.0%			16.0%	

*These compositions fall on the SiO_2 -CA join in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system.

IV. PROPERTY MEASUREMENTS

A. Autoclave Heating Curves

The high pressure autoclave with an inside cylindrical sample opening of approximately 3 inches in diameter and 10 inches in height requires 12 to 24 hours to reach equilibrium temperature. The first seven hours recording the inside and two outside temperatures are given for a furnace temperature setting of 600°C in Fig. 4. Figure 5 shows the amount of temperature differential between the inside and outside temperatures. The temperature differential increases to a maximum amount of ~50 °C at a furnace setting of 500°C.

B. Permeability Measurements

1. Standard Medium Pressure Cell

Permeability of three hydrothermally-treated Unadeep and Secar-cement samples were measured and are shown in Fig. 6. Pressurized nitrogen gas was forced through the samples using a standard medium pressure cell. In this pressure cell the samples may be either 0.875 or 1.00 inches in diameter; the thicknesses range from about 0.50 to 2.00 cm.

The permeability of Unadeep cement sample #6 gave identical permeability for both direct and reversed nitrogen flow direction. The agreement between the two sets of values shows the degree of reproducibility of the system. The permeability for this sample was 1.10×10^{-4} Darcys.

Both the Secar cement samples HYD-1 and HYD-2 are of the same composition but had different curing times. The permeability of HYD-1 (1S) was reported in the December monthly report as 1.45×10^{-5} Darcys but this was found to be in error. Originally the top and bottom surfaces of the sample were not coated with epoxy where they came in contact with the O-rings and only the area within the O-rings was used as the effective area in the calculations. These two changes resulted in a lowering of the effective permeability of about 25%. The permeabilities of the HYD-1 and HYD-2 samples were 1.20×10^{-5} and 1.10×10^{-5} Darcys respectively. A slightly higher permeability value was obtained from the sample cured for a longer period. This may have occurred because wairakite occurred in the reacted sample, or may reflect compositional differences.

Figure 4. Heating curves for autoclave.

Figure 5. Relationship between inside and outside temperature for autoclave.

Figure 6. Comparison of permeability between the Unadeep and Secar-cement samples.

2. Hoek-Franklin Cell

We have begun using a Hoek-Franklin permeability cell which allows for lateral confining pressures of up to 5000 psi (34.5 MPa) while measuring gas flow through the sample. The outer surface must be clean and defect-free. Of the three samples reported above, only the HYD-2 sample was prepared in such a fashion that allowed a permeability measurement to be obtained with a confining pressure in the cell. Figure 7 is a comparison of these two data sets. The value of 1.85×10^{-4} Darcys presented here was measured with a confining pressure of 4000 psi (27.6 MPa). Permeabilities were obtained as the confining pressure was cycled down to 1500 psi (10.3 MPa). The permeability values obtained for these measurements increased slightly.

The order of magnitude difference between permeability measured with these two different cells is certainly unacceptable. The reason for the disparity can be tentatively explained. The sample possessed a crack that was about 1.0 cm across; the crack continued diagonally through the sample some unknown distance. It is felt that this open pathway was sufficiently closed by the confining pressure to allow a permeability measurement that approached to within an order of magnitude of an acceptable value. The problem of initial uniaxial loading of the samples in the cell had caused considerable difficulty before it was recognized and loading procedures modified to accommodate it.

C. Viscosity Measurements

Workability and pumpability properties of fresh cement slurries are very complex and important in the cementing of geothermal wells. For analysis of the properties of fresh concrete it is considered very effective to use a co-axial rotational viscometer for some of the characteristic measurements. Therefore a Brookfield Rheolog model 5X HBT has been put into operation and calibrated.

The output of the viscometer (in millivolts) is proportional to the rotating speed (shear stress) for each spindle when the fluid is Newtonian. For Newtonian fluids the output from spindles #2, 3 and 4 are 1/4, 1/10 and 1/20th that from spindle #1 respectively. One liter of standard paratone

Figure 7. Comparison between the Hoek-Franklin Permeability Cell and the Standard Medium Pressure Cell.

oil was used to calibrate the four spindles. Each spindle was set at the center of a one liter beaker. The output from the Rheolog in Fig. 8 shows a linear relationship suggesting that the viscometer works well and that the assumptions in determining viscosity were valid. The mean value of viscosity was 16800 centipoise (cp). When the viscosity measurements were made before the oil had a time to settle and when the output was less than 10% of full scale then the data had more scatter. The remaining 9 values, which were obtained by different spindles and different rotating speeds were within the viscosity range of 16800 ± 500 cp. This viscosity is within the expected range of measurements for cement pastes according to some work being done at Oak Ridge National Laboratory. An additional viscosity measurement was made on standard mineral oil with a known viscosity of 340 to 365 cp which was measured as 240 to 352 cp at 25°C. This is also within the calculated error of expected accuracy.

For these Newtonian fluids the output became stable within a very short time with no hysteresis. In addition, viscosities of these fluids are constant over time and produce constant viscous shear over time.

On the other hand, the viscosity of a cement paste changes with time and produces an "exponential-decay-type curve as shown in Fig. 9. The viscosity for a cement paste is more difficult to calculate. Murata and Kikukava (1973) assumed the flow of fresh cement slurries to be similar to a Bingham Fluid with a linear relationship between viscosity and shear stress after 60 minutes of mixing. The slope of the linear portion of the curve is called the plastic viscosity, η_{pl} . They recommended a small plastic viscosity, for a better pumpable product.

To evaluate the performance of the viscometer with cement pastes the following procedure has been established:

- prepare pastes according to ASTM C-309.
- after completion of mixing, a 3 minute rest period is allowed with bowl covered.
- this is followed by a 5, 15 or 25 minute slow mix period with the mixer set at slow speed.

Figure 8. Viscosity measurements on Paratone Calibration Oil.

- two minutes are allowed for transfer of the paste to a 600 ml beaker and to set up the viscometer.
- a one-minute measurement is taken at 100 rpm, then 20 - 30 second measurements at 50, 20 and 10 rpm, sequentially.
- a one-minute delay period, followed by increase in shear rate at 20 second intervals.

D. Microhardness and Compressive Strength Measurements

Microhardness measurements using a Leitz miniload microhardness tester was used with a 40X objective to yield hardness values based on the Vickers method. Table 3 lists the actual microhardness measurements; Table 4 is a summary of all the data that have been measured on the geo-thermal cement products thus far.

Figure 9. Rheological measurements on a cement paste.

Table 3
Microhardness Compressive Strength and Bulk Density Measurements
for Secar and Unadeep Cements and Type V Cement + Melment Additives

Sample	Trial #	diagonal 1		diagonal 2		Weight (pond)	Bulk Density (g/cc)
		reading	HV (kg/mm ²)	reading	HV (kg/mm ²)		
<u>Compressive Strength = 311 kg/cm²</u>							
HYD-1	1	118.3	39.95	118.5	39.6	300	1.33
50% Secar cement	2	112.5	43.95	110.7	45.6		
50% Minusil	3	117.5	40.3	118	40		
Cured 60 hours	4	117	40.6	119	39.3		
400°C	5	116.7	41.0	119	39.3		
1400 psi	6	194	14.78	191.5	15.25		
w/c = 0.4	7	144.5	26.8	142.5	27.39		
	8	178	17.55	175	18.16		
	9	157	22.6	158	22.28		
	10	171	19.02	175	18.16		
		mean		= 30.66			
		std. dev.		= 11.55			
<u>Compressive Strength = 306 kg/cm²</u>							
HYD-2	1	150	24.7	150	24.7	200	1.43
50% Secar cement	2	206	13.11	212	12.38		
50% Minusil	3	225	10.99	221	11.39		
Cured 156 hours	4	179	11.57	184	10.95		
325°C	5	146.5	17.28	149	16.7		
1400 psi	6	125	23.7	127	23		
w/c = 0.4	7	164.5	13.7	163.5	13.87		
	8	137	19.76	131	21.6		
	9	125	23.7	127	23		
	10	178	11.7	181.5	11.26		
		mean		= 17.02			
		std. dev.		= 5.54			
<u>Compressive Strength = 341 kg/cm²</u>							
10% MgO + Unadeep	1	194	9.85	198	9.46	200	1.48
Cured 10 days	2	168	13.14	174	12.25		
400°C	3	178	11.7	185	10.83		
8000 psi	4	203	9.0	200	9.27		
	5	182	11.19	175	12.11		
	6	175	12.11	173	12.39		
	7	115	28	118	26.6		
	8	105	33.6	103	35		
	9	125	23.7	123	24.5		
	10	97	39.4	94	42		
		mean		= 19.17			
		std. dev.		= 11.12			
<u>Compressive Strength = 688 kg/cm²</u>							
7% Melment	1	125	35.6	125	35.6	300	
Cured 4 months	2	103.5	51.9	110	46		
(October 4, 1977)	3	104	51.4	105.5	50		
25°C	4	108.5	47.7	109.5	46.4		
14.7 psi	5	111.5	44.7	110	46.0		
	6	104.3	50.9	109.5	46.4		
	7	106	49.5	104	51.4		
	8	100	55.6	105	50.5		
	9	102	53.5	102	53.5		
	10	103	55.6	103	55.6		
		mean		= 49.64			
		std. dev.		= 5.97			
<u>Compressive Strength = 708 kg/cm²</u>							
5% Melment	1	116.5	41			300	
Cured 4 months	2	102	53.5				
(October 4, 1977)	3	102	53.5				
25°C	4	116	41.3				
14.7 psi	5	135	30.5				
	6	102	53.5				
	7	100	55.6				
	8	102	53.5				
	9	100	55.6				
	10	103	52.4				
		mean		= 49.04			
		std. dev.		= 8.47			

Table 3 (Continued)

Microhardness Compressive Strength and Bulk Density Measurements
for Secar and Unadeep Cements and Type V Cement + Melment Additives

Sample	Trial #	diagonal 1		diagonal 2		Weight (pond)	Bulk Density (g/cc)
		reading	HV (kg/mm ²)	reading	HV (kg/mm ²)		
Compressive Strength = 203 kg/cm ²							
#6	1	156.3	15.18	}		200	1.457
67% Unadeep	2	175	12.11				
23% Minusil	3	199	9.37				
10% MgO	4	150	16.48				
	5	153.5	15.74				
	6	192	10.06				
	7	188	10.49				
	8	192	10.06				
	9	175	12.11				
	10	140.5	18.79				
		mean = 13.04					
		std. dev. = 3.27					
Compressive Strength = 163 kg/cm ²							
#6H	1	125	11.87	}		100	1.402
67% Unadeep	2	133	10.43				
23% Minusil	3	131	10.81				
10% MgO	4	143	9.07				
	5	125	11.87				
	6	129	11.14				
	7	124	12.06				
	8	126	11.68				
	9	137	9.88				
	10	141	9.33				
		mean = 10.82					
		std. dev. = 1.10					
#6G	1	140	9.46	}		100	
67% Unadeep	2	139	9.60				
23% Minusil	3	127	11.50				
10% MgO	4	84.6	25.91				
	5	104	17.14				
	6	140	9.46				
	7	126	11.68				
	8	148	8.47				
	9	128	11.32				
	10	136	10.03				
		mean = 12.46					
		std. dev. = 5.31					
#8G	1	148	8.47	}		100	
44% Unadeep	2	132	10.64				
46% Minusil	3	150	8.24				
10% MgO	4	145	8.82				
	5	175	6.06				
	6	147	8.58				
	7	130	10.97				
	8	130	10.97				
	9	137.5	9.88				
	10	128.5	11.23				
		mean = 9.38					
		std. dev. = 1.65					

Table 4

Summary of Data Measured on
Geothermal Cement Products

Sample	Composition	Hydrothermal Treatment	Length (inch)	Diameter (inch)	Weight (g)	Compressive Strength (kg/cm ²)	Micro-hardness (std dev) (kg/mm ²)	Bulk Density (g/cc)	He Density Pycometer (g/cc)	Permeability (Darcys)
HYD-1	50% Secar 50% Minusil w/c = 0.40	1400 psi 400°C 60 hours	20.5/32	32.0/32	dry: 12.72	311	30.66	1.33		1.10 x 10 ⁻⁵
HYD-2	50% Secar 50% Minusil w/c = 0.4	1400 psi 325°C 156 hours	23.0/32	32.5/32	dry: 11.579 sat: 14.38	306	17.02	1.43		1.20 x 10 ⁻⁵
3A	54.5% Unadeep 20.5% Minusil 25% MgO	9000 psi 400°C 9 days				75		1.902		
3B	54.5% Unadeep 20.5% Minusil 5% MgO w/c = 0.49	9000 psi 400°C 7 days				61		1.920		
5U	84% Unadeep 16% MgO w/c = 0.41	5000 psi 128°C 10 days				145				
5	90% Unadeep 10% MgO w/c = 0.32	8000 psi 400°C 10 days	48.5/32	28.0/32	dry: 22.04 sat: 28.06	341	19.17	1.480	2.038	
6	67% Unadeep 23% Minusil 10% MgO w/c = 0.467	10000 psi 400°C 23 days	44.5/32	28.0/32	dry: 19.32 sat: 23.55	203	13.04	1.457	1.73	1.10 x 10 ⁻⁴
6H	67% Unadeep 23% Minusil 10% MgO	10000 psi 400°C 23 days	43.7/32	28.0/32	dry: 18.68 sat: 23.47	163	10.82	1.402	1.71	
6G	67% Unadeep 23% Minusil 10% MgO w/c = 0.41	10000 psi 400°C 26 days					11.27 (2.55)			
8G	44% Unadeep 46% Minusil 10% MgO w/c = 0.41	10000 psi 400°C 26 days					9.56 (1.17)			

V. PERSONNEL

The research for this period has been under the direction of Dr. Della M. Roy with assistance from Drs. R. Smart and E. L. White. A graduate student, C. Langton, and research technicians G. Zimmerman and D. Wolfe-Confer, have been involved in the research to various extents.

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Appendix 7

SOUTHWEST RESEARCH INSTITUTE

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HIGH-TEMPERATURE MATERIALS FOR USE IN THE CEMENTING OF GEOTHERMAL WELLS

TECHNICAL PROGRESS REPORT NO. 2
January - March, 1978
SwRI Project No. 02-5083

to

Brookhaven National Laboratory
Upton, L.I., N.Y. 11973

April 17, 1978

APPROVED:

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ABSTRACT

A program for the development of a high-temperature geothermal-well cement was started October 1, 1977. In this, the second quarter, a continuing review was made of the literature on geothermal-, oil-, and gas-well cements and cementing. Research on Southwest Research Institute's hydrothermal cement formulations has been ongoing to develop pumpability criteria above 425°F (218°C). Work accomplished during the period January 1, 1978, through March 31, 1978, is described in this Second Technical Progress Report.

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I. INTRODUCTION

In October 1977, Southwest Research Institute began a research program to develop an improved cement for use in high-temperature geothermal wells. This report describes the research carried out during the second quarter of the Brookhaven National Laboratory Contract No. 427964-S.

During the period of January 1 to March 31, 1978, a continuing review was made of background data, including published material and SwRI data. Evaluation of a considerable amount of collected information dating prior to 1970 was made. A large number of SwRI cement formulations have been examined. Many screenings have been made and physical testing performed to determine suitability of the particular cement for use above 450°F (232°C). Cement formulations curing at 600°F (316°C) were examined, and several have been selected for further screening. Only consistometric tests have been performed on the cement formulations for use above 600°F.

The general test matrix, particularly concerning the long-term tests, has been somewhat behind schedule during the last month because of equipment failures. These tests will be on schedule, it is hoped, during this coming quarter. Compressive strength, bond strength, and permeability tests on a short-term basis have been made. Tests on the compatibility of the cement with drilling muds and other materials have been completed on the 425°F cements.

II. LITERATURE REVIEW AND EVALUATION

Titles and abstracts of some 2,000 references pertaining to geothermal-, oil-, and gas-well cements, hydrothermal cements, and well completion methods were examined during the past quarter. These references date back to at least 1900; however, most of them have been included in other books and articles both on geothermal, oil, and gas wells. Dwight Smith includes many of these references in his book on cementing. With this in mind, a second major bibliography will not be undertaken in this quarterly report. It is probable that at some future date this material will be assembled into an annotated bibliography on geothermal well completion practices.

As a part of the data review and evaluation phase of our study, Mr. W. A. Mallow attended the Corrosion '78 Conference in Houston, Texas, on March 6-10. Four of the papers he heard dealt with problems encountered in geothermal wells. Presentations reviewed at the NACE meeting included "The Role of Chemical Components in Geothermal Fluids on Corrosion," by Donald W. Shannon of Battelle Pacific Northwest Laboratories. In this paper, Shannon surveyed the effect of pH, temperature, salinity, dissolved CO₂, H₂S, and silica on corrosion of carbon steel and alternate alloys. The roll of film formation in corrosion was also reviewed. As expected, carbon steel corrosion increases rapidly as pH drops below 5 and at greatly accelerated temperatures of 250°C and 20% sodium chloride. The contribution of dissolved silica and the possible formation of iron silicate was not conclusive. More testing is required to determine this. Specimens were submitted to actual field conditions in the East Mesa No. 6-1 geothermal well located near Holtville, California. Only preliminary data were available for this presentation. Good correlations were reported between laboratory

experiments at 150°C and the natural-brine environment. There was reduced corrosion in the actual geothermal fluid at 50°C. This may be due to a silica film that deposited and became rate-controlled.

A second paper titled, "Observations on Materials Exposed to Geothermal Steam at Cerro Prieto," by S. Toney, et al, reviewed the effects of geothermal environment on turbine alloys. Tests were performed to determine corrosion rates over a period of approximately two years and the susceptibility of the turbine alloys to stress cracking and corrosion-pitting attack. The conclusions given are that corrosion rates for turbine alloys are generally low, and that the primary geothermal steam contaminant largely responsible for the corrosion stress cracking of the alloys is sulfide.

A third paper, "Corrosion by Geothermal Fluids in Cerro Prieto," by Sergio Mercado, explores the effect of the geothermal fluids on production equipment. Of particular interest was the concrete which they had coated originally with a coal-tar epoxy. After two years of operation, loosening of the epoxy coating and attack of the concrete in the upper part of the channel was noted. After four years, the attack had become so extensive that the cement was degraded and sand and gravel were dislodged. Mercado claimed that the corrosion was present principally on the channel ceiling caused by H₂S steam and an aerobic bacteria.

The fourth paper was titled "A Downhole Technique for Investigating Cathodic Protection Effects on Well Casings," by Maurice A. Riordan. This paper reviewed the use of a downhole tubing contactor to obtain data that are essential to the determination of a number of criteria outside the production tubing. Not only are downhole data invaluable in the development of a solution to the well casing problem, but these data are also useful in

providing circumstantial evidence that the required electrochemical changes have been effective. It is claimed that some of this information can be correlated to corrosion on the outer surface of the tubing by deduction means.

III. SOUTHWEST RESEARCH INSTITUTE'S HIGH-TEMPERATURE CEMENT RESEARCH

A. General

Selection was made of a hydrothermal cement formulation which would provide adequate pumpability, setting time, and strength at 425°F (218°C). This cement is a slightly modified formulation which is described in detail in SwRI Technical Progress Report No. 1, Reference No. 36 (Mallow and Dean). Physical testing, as described below, has proven that this cement should be adequate for use in geothermal wells with temperatures of at least 425°F. It would be sufficient at higher temperatures if the total time and higher heat flux seen by this cement was for only a very short time.

Many other formulations for use at 600°F (315°C) have been made and autoclaved. As of this report, only the formulation containing zirconia has been successfully run in the consistometer at a temperature of 600°F.

B. Test Matrix

1. Placement Ability

Consistometric tests for the 425 cement have been completed. These tests were based on the API scale of 100 units of consistency being sufficient to indicate thickening. At 425°F (218°C), the average time to 100 units of consistency was four hours. This completes our qualifying tests for the lower temperatures; however, we are first running the higher temperature formulations at 425°F to insure that we have a nonsetting cement.

To date, we have the zirconia formulation which will not thicken in over seven hours at 425°F. The cement does harden at 600°F; however, because of equipment difficulties at this temperature, we have been unable to determine how long it remains pumpable. Work is continuing to determine

placement ability at the higher temperatures with modification to the formulas as needed.

2. Compressive Strength

Small cubes have been made of the various formulations, cured for 24 hours, and tested in a Model No. 977 Instron Load Cell Testing Machine. Strength tests to date have been consistently above 3500 psi (24,000 kPa). Testing of materials cured at higher temperatures is being done presently. Compressive strengths of 3200 psi (22,000 kPa) were recorded for three cubes of the 425°F cement which had been thermally aged 14 days. We are presently running tests on other thermally aged cubes.

3. Bond Strength

We are still running the preliminary bond strength tests on all of the 425 and 600°F cement formulations. No data are available at this time. The first test on bond strength indicates that we will probably get about 1000 psi (6900 kPa).

4. Permeability to Water

The first three permeability tests on our 425°F formulation had given us an average of 2.2 millidarcy (md). Subsequently, we have run permeability tests on our 425°F formulation, and we are now getting an average of .3 millidarcy. We are confident that we will be able to lower this and probably get below the .1 millidarcy permeability required, by using various types of filler material to close the interstices.

We now have our own permeameter, so this work will proceed rapidly in the future. We still have quite a number of permeability tests to perform, particularly on the thermal aging specimens. These specimens were to be aged at 7, 14, and 28 days.

5. Compatibility with Drilling Muds and Drilling Mud Additives

These tests are being performed to determine the compatibility of our cement systems with a number of different drilling fluids commonly used in the drilling of geothermal wells. It is going to be important that we determine the effects of these additives on the cements. If the well, prior to cementing, is not completely cleaned out, there is always a residue on the walls of the formation and on the tubing. This may or may not affect the proper setting and hardening of the cement.

As of this report, 15 compounds, mostly obtained from Baroid Company, were used to determine the cement compatibilities. In the evaluation system given on the next page, we have used the following notations:

- C = Compatibility has been confirmed by actual test
 with this agent;
- AC = Compatibility has been deduced by previous ex-
 perience with these classes of agents and the
 cement constituents;
- I = Incompatibility determined by actual test with
 this agent;
- NR = Not recommended as interface to hydrothermal
 cement except in very dilute concentrations.

TABLE I. COMPATIBILITY OF DRILLING MUD ADDITIVES WITH
SwRI HYDROTHERMAL CEMENT (425°F FORMULATION)

Product Name	Description	Additions (pounds per barrel)	SwRI Rating
AQUAGEL	Sodium montmorillonite powder, nontoxic, S.G. 2.7	10-25	C
BAROID	Barite, barium sulfate powder, BaSO ₄ , S.G. 4.2	50-90	C
CARBONOX	Lignitic humic acid powder, nontoxic	0.5-35	AC
Caustic Soda	Sodium hydroxide flake toxic, NaOH	0.1-3	NR
CC-16	Solubilized sodium salt of lignitic humic acid powder	0.5-6	AC
Gypsum	Calcium sulfate powder, non- toxic, CaSO ₄ ·2H ₂ O	2-6	NR
Lime	Calcium hydroxide powder, Ca(OH) ₂	1-5	NR
OMC	Oil Mud Conditioner	2-4	C
PETROTONE	Organophilic clay powder for use as oil mud suspending agent	0.5-5	C
Q-BROXIN	Ferrochrome Lignosulfonate powder	1-20	C
QUIK-GEL	High yield bentonite	5-10	C
Salt	Sodium chloride granular nontoxic NaCl	5-125	C
Soda Ash	Sodium carbonate powder, Na ₂ CO ₃	0.5-2	NR
Sodium Chromite	Sodium chromate powder, toxic, Na ₂ CrO ₄	0.1-4	NR
ZEOGEL	Attapulgate powder	10-20	C

C. Future Work

During the next quarter, we will be well into the consistometric testing of our higher temperature 600°F cements and, hopefully, on up to the 700°F level. We will, of course, be running our thermal aging tests in the brine and steam conditions, with several curing ages. These tests are underway now, and we will have some results soon. We also will have a number of bond strength tests under thermal aging conditions completed. As fast as the specimens come out of the autoclaves under the curing conditions, we also will be running permeability to water tests. Many corrosion coupons have been set up and also will be tested in the next quarter.

For many of our thermal aging tests, particularly at the higher temperatures, we have determined that our best method will be to place our cement recipe in a small test cell approximately 1 inch by 4 inches long. These test cells are made of rigid copper tubing capped at the bottom, filled with our cement recipe, capped at the top, and placed in the autoclave at the required temperature and conditions for thermal aging. After curing, these specimens will be removed and cut away from the copper tubing for compressive tests.