CEMENTING OF GEOTHERMAL WELLS

PROGRESS REPORT NO. 9
APRIL - JUNE 1978

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Foreword

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 April 1 - June 30, 1978 is described in the current report.

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.

Work on the first element of the program management plan (problem definition) has been completed by Dowell and a report issued. The materials development and property verification phases of the plan are in progress.

The first meeting of the "Geothermal Well Cement Advisory Panel" since it became affiliated as a Task Group of the American Petroleum Institute was held on June 20-21, 1978. All segments of the well completion industry were present at the meeting. The agenda for the meeting included technical presentations by the participants in the materials development and property verification phases of the program, a general discussion of the work and problems associated with the use of the technology by industry, and a visit to an oil well site.

Work on PC containing mixtures of organosiloxanes and styrene is continuing to show the potential of the system as a high temperature cementing material. Samples exposed for 360 hr to brine at 250°C have not shown evidence of hydrolysis and have maintained high strength. At 350°C, the compressive strength is > 5000 psi. Preliminary tests to determine the pumpability of the system are in progress.

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.

Based upon preliminary results from the program, workers at the Los Alamos Scientific Laboratory have requested assistance in the selection of a material for use in the remedial cementing of a hot dry rock well. As a precursor to the selection of a material, property verification tests on several candidate materials will be started at the National Bureau of Standards in August. Cements to be tested include a hydrothermal cement, two polymer cements and a Type G modified with silica flour. A recommendation for a material will be made in late October. The remedial cementing is scheduled for late 1978. If implemented, this will represent the first down-hole test of a cement developed in the program.

Cementing of Geothermal Wells

Progress Report No. 9

April - June 1978

Introduction

The U. S. 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 strength, > 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 prolonged exposure at 400°C 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. Noncorrosive to steel well casing.

The Process Sciences Division of the Department of Energy and Environment at BNL is assisting the Division of Geothermal Energy (DGE) 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. Establishment of 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 are being achieved by performance of the following tasks: 1) development of well-cementing materials capable of withstanding the environmental conditions in geothermal wells, 2) performance of pilot-scale testing and analysis of the cementing materials at well down-hole conditions, 3) development of the technology required to mix, pump, and place the cementing materials, 4) demonstration of the process by the cementing of prototype wells, 5) performance of cost analyses to determine the economic viability of the cementing systems under investigation, 6) involvement of 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, and 7) preparation of a comprehensive,

high-temperature geothermal well-cementing manual which will include details of down-hole 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 ninth in a series of quarterly reports describing work on the program. Accomplishments during the period April-June 1978 are summarized below. During the quarter work has continued in Tasks 1, 2, 3, 4, and 7. Work on 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. The tests 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. Plans are being formulated for down-hole testing. 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 to assist in the technology transfer process and in the establishment of standards, BNL organized a "Geothermal Well Cement Advisory Panel" which was subsequently affiliated with the American Petroleum Institute (API) as a Task Group of the Committee on Standardization of Oil Well Cements. The API Committee Chairman is Dr. Frank Shell of the Phillips Petroleum Company. Mr. J. P. Gallus of Union Oil of California is Chairman of the Task Group. The first meeting of the Task Group was held in Tulsa, Oklahoma on June 20-21, 1978. All segments of the geothermal

industry were represented at the meeting. The agenda included technical presentations by the participants in the materials development and property verification phases of the program and a general discussion of the work and the problems associated with the use of the technology by industry.

Problems with producing a new type of cement for geothermal well applications were discussed in detail. The cement manufacturers present indicated that there is currently a shortage of standard oil well cements due to high energy costs, environmental restraints and limited demand. These factors will make it difficult to introduce a small volume specialty cement. Type J cement was mentioned as an example. This material has good high temperature properties but it is now very difficult to obtain. As a result, less effective, but more readily available materials are used.

For inorganic cements, the economics of scale-up are apparent. Therefore, large manufacturing and storage facilities are needed. This is not the case with polymer cements. These cements utilize large volume, commercially available materials which are then mixed to give the proper formulations. It may, therefore, be easier to produce and economically utilize polymer cements rather than inorganic cements in small volume specialty applications.

An invitation was extended to private companies for the submission of candidate geothermal cements for evaluation by the National Bureau of Standards.

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

During the current report period work was continued on polymer cements (PC) containing organosiloxanes and crosslinked mixtures of styrene (St), acrylonitrile (ACN), and acrylamide (Aa).

In the previous report² Thermal Gravimetric Analysis (TGA) data for the crosslinked system St-ACN-Aa were given. The results indicated that for the temperature range 125° to 200°C the polymer exhibited weight losses of up to ~5%. This was thought to be due to unreacted monomer. In order to confirm this, a TGA study of the effect of polymer particle size on the weight loss was performed. These results, shown in Figure 1, indicated that the polymer started to lose weight at lower temperatures as the particle size was decreased. It appears that the increased surface area allows the unreacted monomer to escape easier. Based upon these observations, work to improve the polymerization yield was started.

Results of tests to improve the thermal stability of a system containing 55 wt% St, 35 wt% ACN, 5 wt% Aa, 5 wt% trimethylolpropane trimethacrylate (TMPTMA), are given in Figures 2 and 3. In these investigations the initiators and curing temperature were varied. The thermal stability of the polymer was established before and after washing in ethanol to remove any unreacted monomer.

The results summarized by the curves identified as No. 1 in Figure 2 indicate higher weight losses for unwashed samples than for

Figure 1. The influence of the polymer particle size on the weight loss of polymer. Particle size (mesh): 1 - medium (88 μm); 2 - smallest (63 μm); 3 - largest (150 μm).

Figure 2. The influence of curing temperature and curing agent on the thermal properties of polymer. Monomer system (wt%): Styrene 55, Acrylonitrile 35, Acrylamide 5, Trimethylolpropane trimethacrylate 5. a. Curing conditions: 52°C-16hr, 150°C-3hr, curing agent: AIBN-0.5 wt%. b. Curing conditions: 52°C-16hr, 150°C-3 hr, curing agent: AIBN-0.5 wt% + DTBP-0.5 wt%. c. Curing conditions: 52°C-16 hr, 105°C-3 hr, curing agent: AIBN-0.5 wt%. d. Curing conditions: 52°C-16 hr, 105°C-3 hr, curing time: AIBN-0.5 wt% + DIBP-0.5 wt%.

Figure 3. Infra-red spectra of polymer systems.
 — before washing in ethanol; — — — after
 washing in ethanol; —·—·— filtrate; a, b, c,
 d - same as in Figure 2.

washed samples (curve No. 2). Further improvements in stability can be gained by increasing the final temperature in the two-stage curing process from 105°C to 150°C and by the use of a mixture of two initiators, AIBN and DTBP. These results are also summarized in Figure 2.

The infra-red (IR) spectras for these systems are given in Figure 3. The decrease in the absorption peak for the polymer after washing with ethanol and the occurrence of the same peaks in the filtrate varify the presence of unreacted monomer. The IR spectra also indicate that the use of the mixture of two initiators (curves b and d) to cure the monomer system increased the absorption peaks at 2238 cm^{-1} and in the range $3400\text{--}2900\text{ cm}^{-1}$. These correspond to increases in $\text{C}\equiv\text{N}$ groups and styrene, respectively, and indicate increased conversion. A similar effect was apparent when the temperature of the final curing cycle was increased to 150°C.

Autoclave testing of PC samples containing St-ACN-Aa-divinyl benzene (DVB) mixtures is continuing. Data for exposure times up to 120 days in 25% brine at 238°C are available. Compression strength measurements are being made at ambient temperature and at 150°C. These data are summarized in Table 1. All of the samples had initial strengths at room temperature > 25,000 psi. A sample containing 50 wt% St, 35 wt% ACN, 5 wt% Aa, 10 wt% DVB exhibited essentially no change in strength after exposure to 25% brine at 238°C for 120 days. Samples tested at a temperature of 150°C after exposure to that environment for 120 days had a compressive strength of 21,463 psi.

Work on PC containing silicones was started during the previous report period. To date two organosiloxane materials, Union Carbide

Table 1

Compressive Strength of PC After Exposure to
25% Brine at 238°C

Monomer composition, wt%				Compressive strength, psi, after				
St	ACN	Aa	DVB	preparation	30 days in brine		120 days in brine	
52.5	40	5	2.5	27,788 ^a	30,726 ^a	18,590 ^b	23,334 ^a	18,547 ^b
62.5	30	5	2.5	29,358	32,927	20,577	25,364	19,786
50	40	5	5	27,478	28,440	21,891	21,368	19,722
50	37.5	5	7.5	25,619	34,381	24,103	25,790	21,808
50	35	5	10	26,217	34,466	23,483	33,632	21,463

Monomer concentration, 13 wt%

Polymerization initiator, 0.5 wt% AIBN

a, tested at room temperature

b, tested at 150°C

St, styrene

ACN, acrylonitrile

Aa, acrylamide

DVB, divinyl benzene

Y-9208 and Rhodia Corporation RZ, have been used. These materials contain varying amounts of vinyl groups. A methyl silicon material called V47 has also been used. Styrene, methyl methacrylate and divinyl benzene are added as comonomers in order to produce a three-dimensional polymeric structure. The systems are polymerized using the initiator di-tert butyl peroxide. The resulting linkages between the polymer chains involve the interaction of methyl and vinyl groups. Linkages such as $\text{SiCH}_2\text{CHMeSi}$ and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ may be formed. Methyl silicone fluids which contain difunctional units Me_2SiO have been used in some of the studies. The resulting materials have excellent thermal stability; relatively small variations in physical properties with temperature and have water repellency.

The Si-C bond is very resistant to heat and in the absence of air is stable to $>350^\circ\text{C}$. Si- CH_3 bonds break in the same temperature range in the absence of air. In air, oxidation of the C-H bonds occur with weakening of Si-C bonds.

Organosiloxanes are chemically resistant, being unattacked by dilute acids, alkalies, and by metals and metal salts. These properties are very important for geothermal applications. Another important property is the small change in viscosity with temperature.

The first phase of the BNL study involved the preparation of PC samples for use in determination of the thermal and hydrolytic stability and the compressive strength. The effects of various monomer additives and the curing conditions were also studied. This phase is essentially complete.

Results from thermal stability tests performed on PC containing a 75 wt% organosiloxane (Y-9208), 25 wt% styrene mixture at 260°C are

Figure 4. Thermal stability at 260°C of PC containing organosiloxane.

shown in Figure 4. The results indicate initial weight losses followed by stabilization after ~250 hr. Compared to previously obtained data for PC containing organic systems (see Figure 5), the organosiloxane PC exhibits considerable improvement.

TGA data for the inorganic and organic polymers are compared in Figure 6. These data indicate that the organosiloxane-styrene polymer is stable to ~350°C.

The compressive strengths of PC containing each of the two polymers as a function of test temperature are also given in Figure 6. In contrast to the PC containing the organic polymer which showed a marked decrease in strength with temperature, the strength of the organosiloxane-styrene PC decreased at a much slower rate. At 350°C, the strength was ~5000 psi.

Compressive strength data for PC containing organosiloxane (Y-9208) and styrene in conjunction with various aggregate compositions are given in Table 2. Strengths before and after exposure for 30 days to brine at 240°C are given. These preliminary results support earlier work² which indicated that the addition of portland cement results in improved durability.

The effect of heating organosiloxane-styrene polymer in air at 260°C is illustrated in Figure 7. Decomposition is apparent after 16 hr.

The use of the same polymer system in conjunction with a 90% sand - 10% portland cement aggregate improves the resistance to oxidation significantly. As shown in Figure 8, PC heated in air for 1500 hr at 260°C had an appearance similar to that of the control.

Some cracking was noted after exposure of the PC to steam at 275°C for 168 hr (see Figure 8). It is believed that this can be corrected by

Figure 5. Effect of temperature on weight loss of the polymer in polymer concrete samples. Monomer system in wt% St-55, ACN-35, Aa-5, TMPTMA-5. (1) 275°C, (2) 240°C.

Figure 6. Polymer weight loss and PC compressive strength at various temperatures.

Table 2

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

Monomer composition, wt%		Aggregate composition, %	Compressive strength, psi	
OS	St		Controls	After exposure for 30 days to brine at 240°C
75	25	100% No. 500 Sand	6,034	5,443
75	25	65% No. 500 Sand-35% Type II Cement	2,924	2,918
75	25	36% No. 16 Sand-17% No. 30 Sand-17% No. 100 Sand-30% No. 50 Sand	5,849	4,200
100	0	Same as Above	1,789	1,150
75	25	90% No. 500 Sand-10% Type III Cement	12,358 ¹	11,150
75	25	95% No. 500 Sand-5% Fe ₂ O ₃	11,084 ²	9,200
75	25	100% No. 30 Sand	689	--
75	25	65% No. 30 Sand-35% Type III Cement	4,588	7,016
75	25	100% No. 100 Sand	370	--
75	25	65% No. 100 Sand-35% Type III Cement	3,160	3,200

OS, Organosiloxane

St, Styrene

1. Boiling water absorption %, 0.33

2. Boiling water absorption %, 0.31

Figure 7. Thermal oxidation degradation of siloxane - styrene copolymer in air at a temperature of 260°C.

Figure 8. PC containing siloxane and styrene after exposure to hot air and steam.

modification of the aggregate composition.

Since the hydrolytic stability of organosiloxanes is of primary importance in determining the potential for their use in geothermal processes, tests were run on two polymers after exposure in 25% brine at 250°C for 360 hr. Two systems, Y-9208 with styrene and RZ to which V-47 was added, were tested. The results indicated no appreciable weight loss or deterioration. IR spectra (see Figures 9, 10, and 11) made before and after the brine exposure indicated the formation of weak peaks in the region 3700-3600 cm^{-1} that correspond to free OH groups. Peaks at 940-930 cm^{-1} and 1650-1600 cm^{-1} which correspond to CH=CH and -CH- groups, respectively, decreased after exposure to brine. These changes were very small.

The small amount of hydrolysis that was detected should be overcome when the polymer is used in PC. If cement is used in the aggregate, the presence of MgCO_3 and CaCO_3 should act as buffers and reduce hydrolysis to essentially zero.

The second phase of the program on organosiloxanes which includes the optimization of the monomer and aggregate systems and determination of the pumpability has recently been started.

Work to optimize the thermal properties of the polymer with respect to composition and curing conditions is in progress. Two organosiloxanes, Y-9208 and RZ, are being used in these studies.

The effect of initiator concentration on the thermal stability of polymer containing 75 wt% Y-9208 and 25 wt% styrene is shown in Figure 12. These results indicate increased stability with increased di-tert-butyl peroxide concentration. At a concentration of 1 wt%, a

Figure 9. Infra-red spectra of polymer before and after exposure to hot brine. Organosiloxane monomer mixture of 75 wt% Y-9208 - 25 wt% styrene. a, after exposure; b, before exposure.

Figure 10. Infra-red spectra of polymer before and after exposure to hot brine. Organosiloxane monomer mixture of 75 wt% Y-9208 - 25 wt% styrene. a, after exposure; b, before exposure.

Figure 11. Infra-red spectra of polymer before and after exposure to hot brine. Organosiloxane mixture of 97 wt% RZ - 3 wt% V47. a, after exposure; b, before exposure.

Figure 12. The effect of initiator concentration and temperature on the thermal stability of polymer. Monomer system 75 wt% organosiloxane Y-9208 - 25 wt% styrene. Initiator di-tert-butyl peroxide.

weight loss of 0% at 300°C was measured on the TGA.

PC samples were made for thermal stability tests using the above monomer and initiator system in conjunction with aggregate containing CaCO_3 , SiO_2 , and Type III portland cement. The results, given in Table 3, indicate that the best results were obtained when an aggregate containing 50 wt% CaCO_3 and 50 wt% cement was used.

Experiments to optimize the RZ-styrene formulation are also in progress. The chemical structure of the RZ organosiloxane is as follows:

where $\text{R}=\text{CH}_3$ and $\text{R}_1=\text{CH}=\text{CH}_2$.

Tests were performed in which 1 mole of the siloxane was copolymerized with various amounts of styrene. The results, shown in Figure 13, indicated that the maximum thermal stability occurred when 3 to 4 moles of styrene are utilized.

The results from a study to determine the effect of initiator concentration on the thermal stability are summarized in Figure 14. As noted in the Figure, increases in concentration beyond 0.5 wt% have little effect on the weight loss of polymer at 250°C or 300°C.

The effect of the addition of the RZ organosiloxane to either the V-47 or the Y-9208 was also studied. Figure 15 summarizes the polymer weight loss as a function of the RZ to Y-9208 ratio at two curing

Weight Loss of Organosiloxane Polymers in PC
at Elevated Temperatures

Monomer composition, wt%			Aggregate composition, wt%			Polymer weight loss ^a , wt%			
OS	St	Initiator	CaCO ₃	Cement	Sand	250°C	300°C	350°C	400°C
75	25	0.5	100	0	0	0	0.1	0.3	1.2
			50	50	0	0	0	0.1	1.2
			25	0	75	0.1	0.1	0.1	0.9

a, measured in nitrogen
OS, organosiloxane
St, styrene
Initiator, di-tert-butyl peroxide

Figure 13. The effect of the addition of styrene to RZ organosiloxane on the thermal stability of the polymer. The siloxane content was 1 mole and the initiator was di-tert-butyl peroxide.

Figure 14. The effect of initiator concentration on the thermal stability of polymer containing RZ organosiloxane and styrene. Initiator, di-tert-butyl peroxide.

Figure 15. The effect of organosiloxane mixtures on the thermal stability of the polymers.

temperatures. The results indicate maximum stability when the concentration of the Y-9208 is in the range 70 to 80 wt%. At these concentrations, the stability was independent of the curing temperature.

When the methyl silicone material V-47 was mixed with the RZ organosiloxane, the maximum stability occurred at an RZ concentration of 97 wt%. This is shown in Figure 16. Increasing the initiator concentration from 0.25 to 1.0 wt% also increased the stability of the polymer. This is shown in Figure 17.

Based upon these results, samples of PC have been prepared for testing at the Los Alamos Fenton Hill site and at the San Diego Gas and Electric Company site at the Salton Sea. These tests are scheduled to start during the next report period.

Preliminary work to determine the pumpability of PC containing organosiloxanes has been started. In this work the time for the unpolymerized material at a temperature of 300°C and pressure of ~ 6000 psi to reach a viscosity of ~ 100 poise, will be measured. If the viscosity can be kept below this level for 3 to 4 hr, consistometer tests will be performed. To date, the high pressure equipment has been assembled and calibrated. Polymerization rate measurements will commence during the next period.

2.2 Aggregate Composition

In the previous progress report² preliminary results were given from differential scanning calorimetry (DSC) and infra-red analysis (IR) studies performed on PC samples containing methyl methacrylate (MMA) and the various constituents of portland cement. These results indicated that the $3 \text{ CaO} \cdot \text{SiO}_2$ (abbreviated form C_3S) component of anhydrous cement had the

Figure 16. The effect of various ratios of RZ and V47 organosiloxanes on the thermal stability of the polymer at 300°C. Initiator, di-tert-butyl peroxide.

Figure 17. The effect of initiator concentration on the thermal stability of RZ and V47 organosiloxanes at 300°C. Initiator, di-tert-butyl peroxide.

greatest effect on thermal stability. This is illustrated in Figure 18. Based upon these observations, it was theorized that an interaction between the calcium oxide and the $-\text{CH}_2-$ groups in the vinyl-type polymers occurs.

During the current report period the work was extended to include styrene, another vinyl-type polymer. Work in which a high temperature polymer system, 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA, was used in conjunction with CaO-SiO_2 and $\text{CaO-Al}_2\text{O}_3$ aggregate systems was also performed. Studies to determine the effect of residual free lime in the CaO-SiO_2 system on the dimensional stability of PC specimens upon exposure to hot brine were also performed. These results are discussed below.

Figure 19 shows the results from DSC studies on PSt and PSt combined with various aggregates. The results for PSt (curve a) indicate the first endothermic peak at $\sim 332^\circ\text{C}$ and a second endothermic peak at $\sim 425^\circ\text{C}$. The first peak is attributed to the thermal decomposition of $-\text{CH}_2-$ groups in the main PSt chain while the second is due to the thermal decomposition of single $-\text{CH}_2-$ linkages within the aromatic ring.³

Curves for PC samples containing 2 CaO-SiO_2 and 3 CaO-SiO_2 (curves c and b, respectively) do not have the endothermic peak at $\sim 332^\circ\text{C}$. Therefore, it appears that the thermal decomposition between the $-\text{CH}_2-$ main chains in PSt is prevented by the presence of C_2S and C_3S .

The results from compressive strength tests performed on PC containing PSt and various aggregates are summarized in Table 4. Each sample with the exception of the control (PC-0) contained 13 wt% polymer, 70 wt% silica sand and 17 wt% of the CaO-SiO_2 or $\text{CaO-Al}_2\text{O}_3$ - containing materials. The results after exposure of the specimens for 30 days to air at 238°C

Figure 18. Methyl methacrylate (left) and PC containing methyl methacrylate and $3\text{CaO}\cdot\text{SiO}_2$ (right) at a temperature of 240°C .

Figure 19. Differential scanning calorimeter thermograms of polystyrene (PSt) samples. a, bulk PSt; b, 34 wt% PSt - 66 wt% $3\text{CaO} \cdot \text{SiO}_2$; c, 34 wt% PSt - 66 wt% $2\text{CaO} \cdot \text{SiO}_2$; d, 50 wt% PSt - 50 wt% SiO_2 ; e, 34 wt% - 66 wt% Al_2O_3 . Heating rate = $20^\circ\text{C}/\text{min}$.

Table 4

Stability of PC Containing $\text{CaO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ Systems After 30 Days
Exposure at 238°C to Hot Air and 25% Brine

Specimens No.	Composition ^a	Before Exposure	After Exposure to Hot Air	Weight	After Exposure to Brine	
		Compressive strength, psi	Compressive strength, psi	loss, %	Compressive strength, psi	Diameter changes, %
PC-0	11% P-89% S	8,850	860	5.20	981	+ 0.26
PC-1	13% P-70% S-17% Cement	10,500	4,100	2.25	4,403	+ 1.88
PC-2	13% P-70% S-17% CaCO_3	10,633	881	3.06	952	- 0.95
PC-3	13% P-70% S-17% SiO_2	3,922	548	7.21	768	- 1.25
PC-4	13% P-70% S-17% Al_2O_3	7,765	684	4.36	1,090	- 0.15
PC-5	13% P-70% S-17% $2\text{CaO} \cdot \text{SiO}_2$	12,436	16,487	0.47	15,270	+ 2.59
PC-6	13% P-70% S-17% $3\text{CaO} \cdot \text{SiO}_2$	18,281	16,276	0.46	16,150	--
PC-7	13% P-70% S-17% $4\text{CaO} \cdot \text{SiO}_2$	17,900	15,826	0.43	-- ^b	--
PC-8	13% P-70% S-17% $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$	13,368	3,217	1.39	3,117	+ 4.08
PC-9	13% P-70% S-17% $3\text{CaO} \cdot \text{Al}_2\text{O}_3$	13,957	6,417	1.16	933	+11.67
PC-10	13% P-70% S-17% $4\text{CaO} \cdot \text{Al}_2\text{O}_3$	14,855	7,061	0.64	-- ^b	--

a, P = 55 wt% styrene - 36 wt% acrylonitrile - 9 wt% TMPTMA; S = 50 wt% #16 sand (size, 1.19 mm) - 25 wt% #30 sand (size, 0.595 mm) - 25 wt% #100 sand (size, 0.149 mm).

b, Failed (large expansion and removed from test).

indicate that the samples containing C_2S and C_3S maintain high strength. All of the other materials exhibited considerable reductions in strength.

After exposure to brine at $238^{\circ}C$ for 30 days, specimens containing C_3S with a free lime concentration of 8.7% could not be tested due to a large expansion due to the chemical reaction between the lime and the brine. However, a sample containing 2% free lime in the C_3S had a strength of 16,150 psi after the brine exposure.

Good durability was also indicated for PC samples containing C_2S (free lime content $\sim 2.7\%$). This material exhibited a 2.59% increase in diameter and had a compressive strength of 15,270 psi.

The effect of free lime content in the $CaO \cdot SiO_2$ compounds on the expansion of the PC after exposure to hot brine is shown in Figure 20. The data indicate that the expansion can be maintained below 1% if the free lime concentration in the $2 CaO \cdot SiO_2$ or $3CaO \cdot SiO_2$ is $< 2\%$.

Currently work is in progress to determine the effect of the aggregate composition on the thermal stability of epoxy, phenol-formaldehyde and furan resins. Evaluation of the bonding structure between PMMA and C_2S by use of scanning electron microscopy is also being made.

2.3 Inorganic Cements

Research on high temperature inorganic cements is in progress at six laboratories. The scope and a short summary of the most recent progress report for each program are given below. The full report is included in the Appendix.

Colorado School of Mines

G. L. Kalousek, Principal Investigator

Starting date, April 1977

Figure 20. Dimensional stability of PC after exposure to hot brine as a function of free lime concentration in C_3S -containing aggregate.

Earlier work at the Colorado School of Mines funded by the National Science Foundation included determination of the chemistry of calcium silicate hydrates and their relation to strength. Out of six different calcium silicate hydrates, with and without modifications with Al_2O_3 over the temperature range of 150° to 345°C , only one, tobermorite, was established as a satisfactory binder, but only up to a temperature of about 150°C . At this and higher temperatures tobermorite transforms to xonolite with serious strength loss and increased permeability. Introduction of 7% Al_2O_3 into the tobermorite lattice stabilized it to a temperature of about 250°C . Another possibly satisfactory binder having a composition of C_2S_3 and containing 5% or more Al_2O_3 was stable over an approximate temperature range of 275° to 325°C . This binder, exhibiting a tobermorite like x-ray diffraction, is of possibly unique mineralogical composition. The Al_2O_3 substituted tobermorite and this phase appeared to merit further detailed study.

The present work is designed with the objective of improving present cements or development of new ones for long-time service and fulfilling fully or partly the following requirements: slurry consistency, early and final strength, compatibility with extraneous constituents, bond formation to steel and wallrock, volume stability, noncorrosion of steel casing and resistance to saline water attack.

The cementitious constituents, at least in the initial stages, will be a C_2S , silica, Al_2O_3 -bearing minerals and other additions. Portland cement which permits only limited control of mineralogical compositions of the binders and is of questionable pumpability at the high temperature will be excluded from the study until the later stages of the

investigation.

During the current report period the research continues to be conducted with two principal objectives: (1) development of binders of improved properties, and (2) determination of the cause of poor or potentially poor performance of binders. Particular attention is being given to bond strength, long-range strength of cement, and effect of slurry weight reducing additions. Calcium silicate cements are of two classifications, portland cement plus silica and $\beta\text{C}_2\text{S}$ plus silica with and without various additions. The important qualities of the $\beta\text{C}_2\text{S}$ - S cements are simplicity of composition, adaptability to "tailoring" binder molecules of exact compositions and high probability that thickening time is controllable with a minimal use of retarders or none. The principal hydration products are CSH(1) or tobermorite, in early periods and lower temperatures, xonotlite and truscottite. The portland cements already containing fixed amounts of extraneous components do not lend themselves to design of exact compositions using additions. The art of controlling the thickening time with retarders is developed to considerable extent but problems still arise, particularly at the elevated temperatures.

The long-term strengths may be predictable from equilibrium data on the binders. A program on the identification and isolation of truscottite and xonotlite in short periods of autoclaving at elevated temperatures is being conducted with the cooperation of Professor Taylor. Reyerite, a K_2O containing calcium silicate hydrate, is suspect of low long-term strength, and is being studied similarly. The results show that truscottite from 0.6 C/S - $\beta\text{C}_2\text{S}$ -S mixes reaches equilibrium in 30 days or less at

temperatures slightly below 350°C, and the 7 day and 30 day strengths are nearly the same. The 0.6 C/S composition from a Class G cement yielded xonotlite plus silica at 350°C in 90 days or less as equilibrium products. This shows the equilibria, truscottite $\rightarrow$ xonotlite + silica is attained more readily with the Class G cement.

The strengths of the Class G-silica cements at 1.0 C/S with and without different additions show satisfactory strengths at 150°, 175°, 250°, and 340°C. A more detailed study on effects of slurry-weight-reducing additions is now underway. The free expansion and shrinkage of the cements with and without additions show that the Class G cements expand up to 0.1% at 250° and 340°C. Flyash, together with perlite and bentonite, caused a 0.2% shrinkage at 340°C.

The β C₂S-S cements show satisfactory strengths and a 0.65 C/S plus 3% Al₂O₃ is being studied in some extent. Additions of Al₂O₃ in larger amounts may cause large shrinkages of the cement. The study of 1.0 C/S β C₂S-S compositions generally gave satisfactory strengths, but nearly all of the modified cements showed shrinkage at 340°C.

Cement-steel and cement-formation bond strengths have been determined using the cement as the annulus between a steel ring and rock or a steel core. The tests at 250°C, mostly on cement showing free expansion, show very high bond strengths. These tentatively are attributed to the compressive stress developed in the cement confined between the steel container and rock or steel core. The tests are being continued at 340°C where relatively large shrinkage occurred. It is expected these results may give some information on the effect of volume change of cement on bond strength.

University of Rhode Island

T. J. Rocket, Principal Investigator

Starting date, July 1977

The research plan is to develop unique phosphate cements which can be used to complete geothermal wells. Using two well proven cement technologies as a starting point, a glass frit is being developed which will react with a buffered phosphoric acid solution to form a calcium aluminophosphate cementing phase. The two established cements that are the starting points for this development program are the phosphate bonded alumina refractory cements used in foundry applications at temperatures in excess of 1100°C and the phosphate bonded glass-frit dental silica cements which have strengths well over 20,000 psi after twenty years in an acid aqueous environment of 38°C .

During the current report period work on $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ systems has been completed. Manuscripts which summarize the findings in both systems have been prepared for publication and are included in Appendix 2. It is doubtful that a cement for geothermal uses could ever be prepared from the CaO system because room temperature reactions are extremely rapid and result in cementing phases which are not stable at 200°C . The two major stable phases present at 200°C are hydroxylapatite and monetite. Neither phase contains much water and the volume changes, as these phases formed would be extreme. There is a better chance to form a cement in a system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. Augellite forms at 200°C and remains stable to at least 400°C . Studies are described in Appendix 2 to test compositions in this system for cements

based on the augellite phase.

Glass corrosion studies of calcium aluminum silicate glasses in phosphoric acid have shown that the set time for a cement can be controlled by controlling the glass composition. For the one to one CaO to Al_2O_3 glasses, solubility rate and mechanism of attack is a function of silica content in the glass. High silica content glasses show virtually no attack by phosphoric acid. Glasses with 40% SiO_2 dissolve homogeneously. There is a range of compositions between these extremes that show ion leaching behavior. These glasses react with phosphoric acid and are replaced by a layer of silica gel which does not react with the phosphoric acid. Solubility rates have been correlated with cementing properties.

As the cement testing continues, work will also continue on the glass corrosion. Further, a study of the phases which are stable at 200°C in the quaternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ is underway.

Dowell Division of Dow Chemical

B. E. Simpson, Principal Investigator

Starting date, July 1977

The Dowell effort is a three-phase program to develop completion systems for geothermal wells. In phase I which has been completed,² a detailed definition of the problem was developed. Phase II is providing an evaluation of the potential systems and the development of the best systems under the criteria developed in Phase I. The goal of Phase II is to develop a safe environmentally acceptable system which will provide both maximum energy recovery and well life. Materials are being examined to determine chemical composition and stability in relation to compressive strengths and permeabilities.

Phase III will be the actual well testing of the materials and systems developed in Phase II.

Phase II of Dowell's DOE contract has continued this quarter with work on the development of a new and improved geothermal cementing system as well as continued effort to build a database of information on systems already in use. After establishment of initial test criteria through geothermal operator surveys, a screening program is well underway to determine the best potential candidates for more rigorous portions of the testing program.

Based on the preliminary results of this screening program, several cementing systems showing promise as potential geothermal cements have been moved into static brine exposure tests to determine their stability under hostile conditions of temperature and chemical environment. In this static testing program cement samples are exposed to synthetic brine prepared to simulate conditions actually encountered in a geothermal well. Early indications are that most Portland-based systems fare quite well in light brines but that severe degradation occurs in many cases when the cements are exposed to heavier brine solutions. The most stable systems in heavy brines appear to be those containing 35 to 40% silica flour (less than 200 mesh). Other silica of a coarser nature does not provide adequate stabilization of Portland systems under heavy brine exposure.

The static tests mentioned above serve as a precursor to more rigorous dynamic brine exposure tests currently in the planning and equipment preparation stages. Dynamic testing will be conducted both in the lab using a geothermal simulator and in the field using actual flowing geothermal

wells located at the East Mesa Test Facility and at the San Diego Gas and Electric Company's facility in southern California. The simulator has been designed by Dowell's chemical and process engineering group and all parts and equipment ordered. It should be on-line by the end of September, 1978.

Chemical studies have centered on the preparation and evaluation of scawtite as a chemical binder in Portland cement due to its chemical similarity to xonotlite, a known binder of high strength characteristics. Initial efforts show that a high concentration of scawtite results in a Portland system when 10 to 25% sodium bicarbonate is added to the mix and that compressive strength appears to correlate with scawtite concentration in a positive fashion.

Further work on a blend of furfuryl alcohol and powdered coal as a non-Portland alternative has continued with emphasis on controlling the large exotherm which results upon polymerization of the alcohol with an acid catalyst. Use of a partially polymerized starting material has reduced the problem considerably and made it possible to measure thickening times for the system.

Battelle's Columbus Laboratories

R. S. Kalyoncu, Principal Investigator

Starting date, September 1977

The objectives of this research program are to evaluate the cementing materials currently used in geothermal applications and, based on the knowledge of this evaluation, to develop new materials which will meet the property requirements dictated by the thermal, mechanical and

chemical environments encountered in geothermal wells.

The work plan of the research program comprises four phases, namely: (1) definition of the current state of knowledge regarding the cementing materials for geothermal applications and selection of materials and screening procedures for determination of the most promising cementing compositions; (2) selection of a list of materials, based on Phase I results, for laboratory evaluation and development and identification of material components most suitable in geothermal applications; (3) further evaluation and development of candidate materials through detailed studies of rheology, compressive strength, permeability, bond strength, compatibility with drilling muds, and characterization of the final products of hydration; and (4) preparation of a final report and the development of plans for further studies. The investigations to date have resulted in significant advances in the evaluation and characterization of promising cementing compositions. A number of compositions made of Class J oil well cement, Silica flour, Blast Furnace slags and pozzolan have been evaluated in terms of their thickening times, strength development, permeability and cement-to-metal casing bond strength.

Cementing compositions with 40% or more cement (Class J, Class H or Class G) had average thickening times at 204°C and 10,000 psi less than two hours. This was somewhat lower than expected as preliminary thickening times were estimated by autoclaving the samples at 204°C to 232°C and saturated steam pressure at these temperatures. After 3 to 4 hours of autoclaving, all of these compositions exhibited consistencies of 100 U_c or below. It was only logical to assume that these compositions would

at least have thickening times of similar magnitude as under static conditions if not somewhat longer. As a result, a number of new compositions with 30% cement have been prepared for evaluation. The thickening times of these compositions are presently being determined.

Outside of the relatively low thickening time values, all the cementing compositions with 30 to 50% cement contents exhibit strengths and other physical properties which meet or surpass requirements.

Pennsylvania State University

D. M. Roy, Principal Investigator

Starting date, September 1977

The program for research to develop new cements utilizable for geothermal wells at temperatures up to 400°C is a two-fold program involving: (1) study to determine the stability of new potential cementing compositions, including investigating optional preparation methods, and performing detailed characterization; (2) determining (for selected potential cementing materials) mechanical and physical properties, and chemical/physical durability under expected conditions when subjected to high temperature and pressure saline solutions or vapors. Compositions will be studied particularly from portions of the following systems, which appear to have considerable potential: $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (high alumina-silica compositions); $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$; $\text{CaO-MgO-SiO}_2\text{-K}_2\text{O-Al}_2\text{O}_3\text{-H}_2\text{O}$.

During the current report period work has continued to obtain more detail on phase stabilities in the low temperature regions for both the lime-magnesia-silica-water and the lime-alumina-silica-water systems. Continued property measurements including microhardness, viscosity and

permeability on the cementitious materials are also reported. Parallel studies have continued using a variety of starting materials including commercial cements and natural mineral additives, with suitable compositional adjustments, and pure chemicals. This approach attempts to define stable equilibria, but apply the results to potential practical systems as quickly as possible.

Southwest Research Institute

D. K. Curtice, Principal Investigator

Starting date, October 1977

Hydrothermally cured cements are being developed for use in geothermal well completion systems. The cure of these cements is controlled by the ambient temperature with the initiation temperature and cure rate being controlled by the chemical composition. The cured elements have high strength, strong adhesion to steel, high temperature resistance, acid and general chemical resistance and other properties which distinguish them from portland or modified portland type cements.

The current program is to first optimize the existing cement formulations for the particular environmental conditions existing in geothermal wells, and then to provide the necessary laboratory test and evaluation program that is necessary to precede a field or downhole test program.

During the current report period selection has been made of several formulations for use over 218°C , and work is continuing to optimize the recipes for use over 315°C . Physical testing of the various formulations has included compressive and bond strengths, permeability to water and compatibility with drilling muds.

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.

Property verification tests on several candidate cements will be initiated at the National Bureau of Standards as a precursor to the recommendation of a material for use in the remedial cementing of a hot dry rock geothermal well at the Los Alamos Scientific Laboratory. Cements being evaluated include a hydrothermal cement, two PCs and Type G modified with silica flour. The test is scheduled to start by mid August.

The test program will consist of the determination of compressive strength, bond strength, and permeability after exposure to water at 200°C. The effect of thermal cycling on bond strength will also be determined.

Task 4. Placement Technology

Work was initiated in this task during the previous report period. To date, thickening time tests have been started on cements identified at Dowell, Battelle's Columbus Laboratories, Southwest Research Institute, and BNL.

Task 7. Administrative

During the current report period, three "Monthly Administrative Letters" were submitted to DGE and Quarterly Progress Report No. 8² was issued. A paper entitled "Polymer Systems in Geothermal Applications" has been accepted for publication in the "Journal of Applied Polymer Science".

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Appendix 1
Fifth Quarterly Technical Report
April 1, 1978 to July 1, 1978
BNL/DOE Contract No. 406003-5
"Development of Cement for Use in
Geothermal and Deep Oil Wells"

ABSTRACT

The research continues to be conducted with two principal objectives: (1) development of binders of improved properties, and (2) determination of the cause of poor or potentially poor performance of binders. Following the report by Dowell, "Development of Geothermal Well Completion Systems" Phase 1, particular attention is being given to bond-strength, long-range strength of cement, and effects of slurry weight reducing additions. Calcium silicate cements are of two classifications, portland cement plus silica and $\beta\text{C}_2\text{S}$ plus silica with and without various additions. The important qualities of the $\beta\text{C}_2\text{S}$ - S cements are simplicity of composition, adaptability to "tailoring" binder molecules of exact compositions and high probability that thickening time is controllable with a minimal use of retarders or none. The principal hydration products are CSH(1) or tobermorite, in early periods and lower temperatures, xonotlite and truscottite. The portland cements already containing fixed amounts of extraneous components do not lend themselves to design of exact compositions using additions. The art of controlling the thickening time with retarders is developed to considerable extent but problems still arise, particularly at the elevated temperatures.

The long-term strengths may be predictable from equilibrium data on the binders. A program on the identification and isolation of truscottite and xonotlite in short periods of autoclaving at elevated temperatures is being conducted with the cooperation of Professor Taylor. Reynerite, a K_2O containing calcium silicate hydrate, is suspect of low long-

term strength is being studied similarly. The results show that truscottite from 0.6 C/S - β C₂S-S mixes reaches equilibrium in 30 days or less at temperatures slightly below 350 °C, and the 7 day and 30 day strengths are nearly the same. The 0.6 C/S composition from a Class G cement yielded xonotlite plus silica at 350 °C in 90 days or less as equilibrium products. This shows the equilibria, truscottite → xonotlite + silica is attained more readily with the Class G cement.

The strengths of the Class G-silica cements at 1.0 C/S with and without different additions show satisfactory strengths at 150, 175, 250, and 340 °C. A more detailed study on effects of slurry-weight-reducing additions is now underway. The free expansion and shrinkage of the cements with and without additions show that the Class G cements expand up to 0.1% at 250 and 340 °C. Flyash, together with perlite and bentonite, caused a 0.2% shrinkage at 340 °C.

The β C₂S-S cements show satisfactory strengths and a 0.65 C/S plus 3% Al₂O₃ is being studied in some extent. Additions of Al₂O₃ in larger amounts may cause large shrinkages of the cement. The study of 1.0 C/S β C₂S-S compositions generally gave satisfactory strengths, but nearly all of the modified cements showed shrinkage at 340 °C.

Cement-steel and cement-formation bond strengths have been determined using the cement as the annulus between a steel ring and rock or a steel core. The tests at 250 °C, mostly on cement showing free expansion, show very high bond strengths. These tentatively are attributed to the compressive stress developed in the cement confined between the steel container and rock or steel core. The tests are being continued at 340 °C where relatively large shrinkage occurred. It is expected these results may give some information on the effect of volume change of cement on bond strength.

Introduction

This report covers continuation of work described in the Fourth Quarterly Report. Additionally, phase identification of potential binders is being done in cooperation with Professor Taylor. Calcium silicate cements in two groups, portland cement-silica and BC_2S -silica, continue to be investigated. Following the report by Dowell, "Development of Geothermal Well Completion Systems," Phase 1, July-Sept. 1977, particular attention is being given to bond-strength, long-range strengths, and slurry-weight-reducing additions. The approach to long-range strength is through the identification of equilibrium phase in cements cured at elevated temperatures for short time and within the temperature stability range of the phases. The research is being conducted with two principal objectives: (1) development of binders of satisfactory properties, and (2) determination of causes of poor or potentially poor performance of binders.

Review of Background on Cements

A summary description of the compositions of the two cements and hydration products is compiled in Figure 1. The important features of the BC_2S -S cement are simplicity of composition, adaptability to "tailoring" of the binder molecules in exact compositions with and without extraneous components (Al_2O_3 , Fe_2O_3 , SO_3 , Na_2O , K_2O , and CO_2) in search for optimum properties and the high probability that the thickening time is controllable with minimal use of retarders or none. The cement consists of BC_2S and S in readily controllable proportions with or without additions in desired amounts. Several binders, depending on composition and temperature-time of autoclaving, may form. The important ones are CSH(1) or tobermorite, at early periods and lower temperatures, xonotlite and truscottite.

The portland cement-silica cement already contains fixed amounts of Al_2O_3 , Fe_2O_3 , SO_3 , Na_2O , K_2O , and other minor constituents. The art of controlling the thickening time of the portland cement with retarders is developed to considerable extent but problems still arise particularly at elevated temperatures. The binders generally are the same as for the $\text{BC}_2\text{S-S}$ cements except at initial periods of curing. In present studies using a Class G cement, $\alpha\text{C}_2\text{SH}$ and $\text{CSH}(1)$ appeared instead of the usual tobermorite or $\text{CSH}(1)$ as with the $\beta\text{C}_2\text{S-S}$ cements. Additionally, the Al_2O_3 and Fe_2O_3 may form separate hydration products or be incorporated totally, or in part, in the structure of tobermorite or xonotlite. The minor constituents can form separate phases as listed in Figure 1, but to date, only K_2O has become suspect as possibly having a deleterious effect on long-range strength.

Attainment of Equilibrium

As reported previously, compositions of 0.6 C/S with and without 5% Al_2O_3 made with the $\beta\text{C}_2\text{S-S}$ cement and autoclaved for 7 to 90 days at 350 °C gave essentially constant strength at 3150 to 3450 psi independently of time of autoclaving or the Al_2O_3 addition. The binders were predominantly truscottite at all periods. More recent detailed studies by Professor Taylor indicate that the truscottite is transforming very slowly to xonotlite at 350 °C. However, it is known that truscottite is the stable phase at some temperature only slightly below 350 °C. Tentatively, it is concluded that the equilibrium phase truscottite was attained at 350 °C between 7 and 30 days. At only slightly reduced temperature, truscottite would remain unaltered as such.

At 0.6 C/S composition of Class G cement and silica autoclaved at 350 °C yielded essentially xonotlite in 30 days with little truscottite,

at 90 days only xonotlite was found indicating attainment of equilibrium at 350 °C in less than 90 days. It appears that 350 °C is close to the transition temperature of the equilibria,

On the basis of these results, it appears that xonotlite is the final product of calcium silicate cements at temperatures at about 350 °C and higher (about 410 °C, depending on pressure). The present results appear promising that calcium silicate-silica cements may give satisfactory strengths over the presently indicated temperature range of geothermal well cements.

The Dowell research on a portland cement-silica-flyash cement of approximately a 0.6 C/S composition showed large strength retrogression in long time tests at temperatures of 232 and 316 °C. A question was raised on long-range strength of such cement. The binder was reported as reyerite (and in later study as a truscottite-like phase). The possibility of the K_2O from the cement and flyash forming reyerite is being investigated in both the synthesis of the phase and its strength.

Class G-Silica Cement Strength and Volume Change

The strengths of the Class G-silica (71 cement: 29S) cements, with and without additions, after curing for 1d at 150 °C, and 7d at 175, 250 and 340 °C are given in Figure 2. The first three results on cement without addition show reasonably fair reproducibility at 150 and 340 °C, but not at 175 or 250 °C. The strengths within the variations appear satisfactory. Strengths of 11,000 - 13,000 psi at 340 °C are unusually high with xonotlite as the dominant and stable phase. The results indicate a high long-range strength for this cement at the high temperatures. Additions of gypsum (2% SO_3) and 1% NaCl had no extensive effect at any of the temperatures.

The additions of slurry weight additions, perlite (P), bentonite (B), gilsonite (gils), and sepiolite (sepi) at W/S (water/total weight of dry solids) of 0.41 to 0.43 caused strength reductions with gilsonite showing the least effect.

In order to prevent formation of $\alpha\text{C}_2\text{SH}$ and $\text{CSH}(1)$ as initial phases, a series of mixes were precured at 23 °C for 24 hours then cured at the higher temperatures. Satisfactory strength was obtained for the cement without addition, but very low strengths prevailed at 23 °C with cement with perlite and bentonite. The 56 cement: 44 flyash (1:1 on volume basis) composition gave low 150 °C strength. Satisfactory strengths developed at the higher temperatures with that at 340 °C being drastically reduced. Addition of 4% perlite + 2% bentonite increased the 150 °C strength, while the other strengths were reduced.

The length changes of representative compositions are given in Figure 3 for the Class G + silica cements with and without additions after a 7-day curing at 250 and 340 °C. The first three results in Figure 3 for cement without addition show reasonably good reproducibility at both temperatures, the volume change was an expansion of about 0.1%. Decreasing the C/S from 1.0 to 0.6 decreased expansion which at 340 °C was close to zero. Additions of gypsum (2% SO_3) and 2% NaCl slightly increased the expansion, all other additions decreased expansion particularly at 340 °C. Addition of 35% flyash, 4% perlite + 2% bentonite caused a 0.2% shrinkage at 340 °C.

Strength and Volume Changes of $\beta\text{C}_2\text{S}$ -S Cements

Earlier tests showed the $\beta\text{C}_2\text{S}$ -S cements were improved by Al_2O_3 . Also, general all around performance was somewhat improved by reduction of the

C/S ratio to 0.65. In Figure 4, strengths are given of 0.83 C/S compositions with and without additions and of 0.65 C/S specimens with special attention to effects of 2.5 to 4.0% Al_2O_3 addition with and without other additions.

As shown by the results, the strengths at 0.83 C/S were satisfactory with and without additions. It should be noted that the 340 °C strengths were substantially lower than the Class G cements. At 0.65 C/S, the effects of Al_2O_3 were determined and the 3% Al_2O_3 content was selected as being close to the optimum. The addition of perlite plus bentonite decreased strength of mixes with increasing Al_2O_3 contents. The 3% Al_2O_3 compositions gave satisfactory strengths; those for the gypsum (2% SO_3) and 1% NaCl additions were excellent at 150 °C showing the accelerating effect of these two salts. Subsequent results show that gypsum (1.0 to 2.8% SO_3) is an accelerator of strength of the 0.65 C/S plus 3% Al_2O_3 compositions at 150 °C.

The general good performance of the Class G + S cement at 1.0 C/S prompted an investigation of the $\beta\text{C}_2\text{S} + \text{S}$ cements at 1.0 C/S. Representative results on mixes with and without various additions of Al_2O_3 and Fe_2O_3 are given in Figure 5. All modifications gave satisfactory strength at all temperatures. These were generally higher than for the Class G + S cements except at 340 °C. The 340 °C strengths were generally lower than at the other temperatures. Gypsum and NaCl has generally minor effect on the strengths, 4% perlite plus 2% bentonite reduced strength substantially at all temperatures. The addition of 2 and 4% Fe_2O_3 as goethite increased significantly the 1 day-strength at 150 °C suggesting it was an accelerator. Later tests using a new sample of Class J cement and goethite did not yield equally high strengths (4300 to 4900 psi).

The dominant binder of both cements at 1.0 C/S was xonotlite, with the β C₂S-S cement containing some scawtite formed from the CO₂ in that cement. There is no basis at present to assume the scawtite caused the lower strengths.

The length changes of β C₂S-S bars at compositions of 0.65, 0.83, and 1.0 are given in Figure 6. The 0.65 C/S composition without addition expanded over 0.1% at both 250 and 340 °C, addition of 3% Al₂O₃ decreased the expansion which was still further decreased to 0.045% at 340 °C by addition of 4% perlite and 1% bentonite. The 0.83 C/S composition (Class J cement) showed substantially less expansion than the 0.65 C/S specimen, which at 340 °C amounted to 0.04% shrinkage. Addition of the optimum amount of Al₂O₃, 7%, to this composition markedly increased shrinkage which was 0.2% at 340 °C. Addition of 4% perlite plus 1% bentonite to the 0.83 C/S composition had no significant effect compared to the specimen without this addition. Gilsonite had a beneficial effect on expansion.

All 1.0 C/S specimens with and without additions underwent shrinkage at 340 °C, and either small expansions or shrinkages at 250 °C.

Cement-Steel and Cement-Formation Bond Strengths

The cement-steel bonds were measured with four cements. The formation-cement tests involved five rocks (granite, sandstone, limestone, serpentine, and basalt) and generally the Class G + S and Class J cements and some modifications of these. The results are given in Figure 7. In this figure, the abbreviations 0.65 and 0.65+A mean 0.65 C/S and 0.65 C/S plus 3% Al₂O₃, respectively, 4P+1B is 4% perlite + 1% bentonite and F-A is flyash.

The results in Figure 7 are only for the 7 day-250 °C cure, only two of these underwent a small shrinkage. The bond strengths independently of rock type or steel or cement were very high. The granite and sandstone were dripped in a bentonite slurry. This treatment reduced the bond strength drastically.

Further tests at 340 °C on cements which undergo large shrinkage at this temperature should reveal if bond strength relates to degree of shrinkage of cement.

Discussions

Bond strengths are expected to relate to expansion and shrinkage of the cement during hydration. Expansion would induce a compressive stress on the cement annulus restrained between the rock and steel casing. Shrinkage would tend to weaken the bond.

Present tests on bond strength at 250 °C showed unusually high shearing stresses for both cement-steel and cement-rock specimens. Nearly all cements showed some expansion and a high bond strength was expected. It is recognized that the cement-rock bond is partly mechanical due to the irregular surface of the rock. Tests now underway at 340 °C on some cements showing high shrinkage should add more information on bond strength as related to shrinkage. Similar tests are also underway using steel cores.

The research at CSM to date shows that, excluding thickening times not yet determined and the still incomplete studies on bond strength, both portland cement-silica and BC_2S -silica cements perform satisfactorily. However, some exceptions to this generalization are indicated in laboratory results as follows:

1. Substitution of 7% Al_2O_3 in tobermorite caused marked increase in temperature stability (to 250 from 150 °C) and in strength. This aluminous tobermorite, however, underwent high shrinkage at 350 °C.

2. Excess Al_2O_3 , 10% or higher, in a xonotlite formulation caused near total loss of strength. Normally such large amounts of Al_2O_3 would not be available except through calcium aluminate cement.

3. The portland cement-silica-flyash cement exhibited high shrinkage, and also in Dowell results, low long-range strength.

4. The possible adverse effect of K_2O on strength is being investigated.

CEMENT

DICALCIUM SILICATE

PORTLAND

COMPONENTS

C, S ADDED SILICA (CO_2)

C, S, A, F, $\bar{S}$, M, N, K
ADDED SILICA (CO_2)

ANHYDROUS PHASES

C_2S , S (CO_2)

C_3S , C_2S , C_3A , C_4AF , $\text{C}\bar{\text{S}}$

HYDRATION PRODUCTS

CSH (1), TOBERMORITE
GYROLITE, XONOTLITE
TRUSCOTTITE, SCAWTITE
("3.15A PHASE")

SAME AS IN C_2S - S CEMENT
AND $\alpha\text{-C}_2\text{SH}$
plus

A - and F - BEARING PHASES
AND MINOR OXIDE PHASES

OTHER PHASES SUBJECT
TO CONTROL BY SELECTED
ADDITIVES

PECTOLITE, 1% N = 11% OF PHASE
REYERITE, 1% K = ~ 67% OF PHASE
ELLASTADITE, 1% $\bar{S}$ = 6% OF PHASE
SCAWTITE, 1% CO_2 = 19% OF PHASE

Figure 1. Summary description of anhydrous and
hydrated phase of portland cement - and BC_2S -
silica cements.

Figure 2. Strengths of class G cement without and with additions.

Figure 3. Length changes of class G cement without and with additions.

Figure 4. Strengths of class J cement without and with additions.

Figure 5. Length change of class J cement without and with additions.

Figure 6. Strengths of class J cements without and with additions.

Figure 7. Bond strengths of cement-steel and cement-rock.

Appendix 2

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

Quarterly Technical Report No. 4
April to June, 1978

from

Department of Materials and Chemical Engineering
University of Rhode Island
Kingston, Rhode Island

to

Process Technology Division
Department of Applied Science
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ABSTRACT

The work on the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and the study of the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ have been completed. Manuscripts which summarize the findings in both systems have been prepared for publication and are included in the report. It is doubtful that a cement for geothermal uses could ever be prepared from the CaO system because room temperature reactions are extremely rapid and result in cementing phases which are not stable at 200°C . The two major stable phases present at 200°C are hydroxylapatite and monetite. Neither phase contains much water and the volume changes, as these phases formed would be extreme. There is a better chance to form a cement in the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. Augellite forms at 200°C and remains stable to at least 400°C . Studies are described in this report to test compositions in this system for cements based on the augellite phase.

Glass corrosion studies of calcium aluminum silicate glasses in phosphoric acid have shown that the set time for a cement can be controlled by controlling the glass composition. For the one to one CaO to Al_2O_3 glasses, solubility rate and mechanism of attack is a function of silica content in the glass. High silica content glasses show virtually no attack by phosphoric acid. Glasses with 40% SiO_2 dissolve homogeneously. There is a range of compositions between these extremes that show ion leaching behavior. These glasses react with phosphoric acid and are replaced by a layer of silica gel which does not

react with the phosphoric acid. Solubility rates have been correlated with cementing properties.

As the cement testing continues, work will also continue on the glass corrosion. Further, a study of the phases which are stable at 200°C in the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ is underway.

I. INTRODUCTION

This report covers the highlights of the research completed under contract BNL 418691-S during the fourth quarter of work from April 1, 1978 to June 30, 1978. Two tasks have been completed. They are the study of the phase relations at 200°C in the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and those in the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$. The results of these studies have been put into two manuscripts which are included as part of this report and which will be submitted for publication upon approval of BNL. These two studies have yielded information basic to the understanding of cementing reactions.

If a phosphate cement is to be used for geothermal purposes a method of controlling setting time must be found. Toward this end, the decomposition of glass by phosphoric acid is being studied. The leaching from a silicate glass of calcium and aluminum ion by phosphoric acid is reported and an observed phenomenon is reported which may act as the setting control mechanism.

Work is underway on the reactions at 200°C in the $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ system. This work is aimed at establishing the potential cementing phases which may exist in this system.

Two avenues of approach are being pursued with regard to cement testing. Various glass compositions are being reacted with phosphate solutions to determine if setting takes place at various temperatures. Also, alumina is being reacted with phosphate solutions at 200°C to see if the phase augelite can act as a stable cementing phase under geothermal conditions.

II. The System $\text{Al}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$

The following is a manuscript to be submitted to the Journal of the American Ceramic Society for publication upon approval from BNL. It summarizes all of the work done on this system under the contract.

These data are now being used as a guide to the design of an aluminophosphate cement for testing under geothermal conditions. The work, based on the discovery of augelite as a stable phase at 200°C , is described elsewhere in this report. The data in the manuscript are also being used in interpreting the reactions in the system $\text{CaO}-\text{Al}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$. The study of this system is also described below.

The System $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 200°C

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ABSTRACT

The 200°C isothermal section was established for the ternary system. Experiments were carried out in sealed glass ampules and phases were identified by x-ray and microscopic techniques. The five solid reaction phases observed were boehmite, $\gamma\text{-AlOOH}$, augelite, $\text{Al}_2\text{PO}_4(\text{OH})_3$, two forms of AlPO_4 -berlinite, the quartz polymorph, and a tridymite form and the aluminum metaphosphate hexahydrate $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$. A maximum of 7 wt% Al_2O_3 can be dissolved in the 70 wt% P_2O_5 phosphoric acid at 200°C.

I. INTRODUCTION

The study of the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ was made as part of an effort to determine if aluminophosphate cements can be used under geothermal conditions. The system is also of

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interest because of phosphate bonded refractories, crystal growth of the piezoelectric, berlinite, and for its mineralogic significance. The literature on the aluminum phosphates and their hydrates is extensive¹⁻⁵ but little is reported at temperatures above 90°C. Table I lists the phases which have been observed in the system and while agreement between various authors is not perfect, the major relationships are well understood. Retrograde solubility is observed for the liquidus surfaces from 25 to 90°C in the low P₂O₅ region⁶ and increasing solubility with increasing temperature is observed for acids greater than 30 wt% P₂O₅. At temperatures above 300°C, Wise and Loh report the stable phases to be corundum, diaspore, AlOOH, berlinite, AlPO₄, augelite, Al₂PO₄(OH)₃ and trolleite, Al₄(PO₄)₃(OH)₃.⁴ Aluminum metaphosphate, Al(PO₃)₃ is also a stable phase.⁷

II. EXPERIMENTAL PROCEDURE

Sixty compositions were studied after firing at 200°C. The compositions are given in Table II. Slurries were made by mixing phosphoric acids, ranging in composition from 2% P₂O₅ (2.8% H₃PO₄) to 52% P₂O₅ (85% H₃PO₄), with either α-Al₂O₃,* or Al(PO₃)₃.* The Al₂O₃ content ranged from 1 to 10 wt%. These slurries were placed in Pyrex[®] glass tubes (20 cm x 8mmOD-5mmID)

* Linde 0.05 micron alumina; aluminum phosphates supplied by Pfaltz and Bauer, Inc.

® Trademark, Corning Glass Works, Corning, NY

so that the tubes were half filled and both ends were sealed. The glass tubes were placed in capped steel pipes to contain fragments in the event of an explosion. Of several hundred runs, two explosions took place and both of these were in runs containing alumina hydroxide and water. Firing times ranged from 1 hour to 590 hours. After each run a vapor phase was present with a liquid phase and, depending upon the equilibrium, one or more crystalline phases were also present in some of the reaction tubes. The vapor phase was saturated air and the internal pressure was calculated to be 250 psi (1,700kPa). Measurement of the Pyrex wall thickness, before and after firing showed no detectable change. The solubility isotherm was determined by direct observation. Clear liquids were examined by microscopy to be **certain no crystalline phase** was present. The identity of crystalline phases in the liquid was determined by x-ray diffraction analysis.

III. RESULTS AND DISCUSSION

The firings made in the system are listed in Table II. The compositions, time of firing at 200°C and phase identified are listed.* Figure 1 is the phase diagram constructed from the data, and Figure 2 shows the phases coexisting with the solutions at the H₂O apex of the diagram.

Two solid phases were found in equilibrium with the acidic solutions. The hexagonal quartz isomorph of AlPO₄,

* Table is available on microfilm from the American Ceramic Society.

berlinite, precipitates from almost all phosphoric acids saturated with Al_2O_3 . Over the range of pure water to 35 wt% P_2O_5 phosphoric acid less than 1 wt% Al_2O_3 is soluble. As the temperature is lowered, the solubility increases. The 35 wt% P_2O_5 phosphoric acid will dissolve up to 6 wt% Al_2O_3 . Maximum solubility occurs at the isothermal-isobaric invariant point located at 7.5 wt% Al_2O_3 : 65 wt% P_2O_5 : 27.5 H_2O at which that liquid coexists with berlinite and a third phase, aluminum metaphosphate hexahydrate. Along the berlinite isotherm, single crystals a millimeter in length were observed.

In the high phosphate region, the primary crystal encountered are hexagonal phase of aluminum metaphosphate hexahydrate, which can be written either as $\text{Al}(\text{H}_2\text{PO}_4)_3$ or $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$. The liquids are extremely viscous and hygroscopic and difficult to separate from the crystal phase which reacts with atmospheric water. Clusters of acicular single crystals grow in radiating clusters in the Pyrex tubes. The crystals grow up to an inch in length. The x-ray diffraction pattern is identical to the one reported by Lehr et al.⁸ The literature suggests that the 1.3.6 and the 1.3.3 phases are both stable at 200°C but the 1.3.3 compound was not observed in any of the firings made.

Figure two shows the solid phases in equilibrium with the solutions in the H_2O region of the diagram. The exact location of the isotherm is not known in this region. The invariant liquid in equilibrium with angelite and boehmite falls above 5% Al_2O_3 . Run 54, the highest alumina run made in this region was still within the two phase region of angelite and

solution (pH=3.5). Small amounts of phosphate ion increase the alumina solubility markedly. Radial crystal masses of an unidentified, probably metastable, aluminum hydrate were observed in runs 30 and 31 after 100 hours. Run 32 yielded boehmite.

The aluminum phosphate hydrate augelite, $\text{Al}_2\text{PO}_4(\text{OH})_3$ is found in several runs as the only crystal phase present and with a tridymite phase of AlPO_4 . This phase could be the basis of a high temperature geothermal cement formed by mixing alumina with phosphoric acid. The final crystalline phase encountered is the tridymite phase of AlPO_4 . The phase is observed in runs after 400 hours and is found just with solution, with augelite and with berlinite. It occurs in the same composition range as trolleite, $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$ a phase which is stable above 300°C ⁴. but was never observed in this study. In pure anhydrous AlPO_4 , the tridymite phase does not form until 820°C . If our observations on this phase represent stability then the substitution of excess aluminum ion and hydroxyl ion in the structure stabilizes the phase to the lower temperature of 200°C .

IV. CONCLUSIONS

Boehmite, augelite, berlinite and a high phosphate phase have been shown to crystallize from aluminophosphate solutions. The solubility isotherm is established at 200°C for most of the system. Further work is necessary to determine the limit of alumina solubility in very low phosphate solutions.

Table I. Solid phases reported in the literature for the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 25, 50, 60, 75 and 90°C. The aluminophosphate hydrates are represented by the number of moles of Al_2O_3 , P_2O_5 and H_2O in each compound.

Temperature °C	Solid phases present	Reference
25	1·1·4, 1·1·7, 2·3·10, 1·3·6	(5)
25	1·1·6, 1·2·9	(2)
50	1·1·4, 1·2·9, 1·3·6	(2)
60	1·1·4, 1·2·5, 1·2·9, 1·3·6	(1)
75	1·1·2, 1·2·9, 1·3·6	(2)
90	1·1·4, 2·3·8	(3)

Table II. Results of experiments made for the system
 $\text{Al}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$

No.	Composition wt.-%			Time Hours	Phases present
	Al_2O_3	P_2O_5	H_2O		
A1	5.0	38.0	57.0	220	$\text{AlPO}_4 + \text{L} + \text{V}$
A2	10.0	36.0	54.0	220	$\text{AlPO}_4 + \text{L} + \text{V}$
A3	5.0	47.5	47.5	220	$\text{AlPO}_4 + \text{L} + \text{V}$
A4	10.0	45.0	45.0	220	$\text{AlPO}_4 + \text{L} + \text{V}$
A5	1.0	49.5	49.5	1.5	$\text{L} + \text{V}$
A6	2.0	58.8	39.2	1.5	$\text{L} + \text{V}$
A7	3.0	58.2	38.8	4	$\text{L} + \text{V}$
A8	4.0	57.6	38.4	9	$\text{L} + \text{V}$
A9	5.0	57.0	38.0	48	$\text{L} + \text{V}$
A10	6.0	56.4	37.6	121	$\text{AlPO}_4 + \text{L} + \text{V}$
A11	4.0	59.14	36.86	46	$\text{L} + \text{V}$
A12	5.0	58.52	36.84	19	$\text{L} + \text{V}$
A13	6.0	57.9	36.1	75	$\text{AlPO}_4 + \text{L} + \text{V}$
A14	7.0	57.29	35.71	75	$\text{AlPO}_4 + \text{L} + \text{V}$
A15	8.0	56.67	35.33	71	$\text{AlPO}_4 + \text{L} + \text{V}$
A16	2.0	49.0	49.0	17	$\text{L} + \text{V}$
A17	3.0	48.5	48.5	22	$\text{L} + \text{V}$
A18	4.0	48.0	48.0	41	$\text{AlPO}_4 + \text{L} + \text{V}$
A19	1.0	39.6	59.4	1	$\text{L} + \text{V}$
A20	2.0	39.2	58.8	50	$\text{AlPO}_4 + \text{L} + \text{V}$
A21	3.0	38.8	58.2	50	$\text{AlPO}_4 + \text{L} + \text{V}$
A22	1.0	19.3	79.2	82	$\text{AlPO}_4 + \text{L} + \text{V}$

Table II. (continued)

No.	Composition wt.-%			Time	Phases present
	Al ₂ O ₃	P ₂ O ₅	H ₂ O	Hours	
A23	2.0	19.6	78.4	93	AlPO ₄ + L + V
A24	1.0	29.7	69.3	93	AlPO ₄ + L + V
A25	2.0	29.4	68.6	93	AlPO ₄ + L + V
A26	1.0	4.95	94.05	312	AlPO ₄ + L + V
A27	2.0	4.9	93.1	312	AlPO ₄ + L + V
A28	1.0	9.9	89.1	312	AlPO ₄ + L + V
A29	2.0	9.8	88.2	312	AlPO ₄ + L + V
A30	2.0	0	98.0	116	Al ₂ O ₃ ·xH ₂ O + L + V
A31	5.0	0	95.0	116	Al ₂ O ₃ ·xH ₂ O + L + V
A32	10.0	0	90.0	116	γ-AlOOH + Al ₂ O ₃ ·xH ₂ O + L + V
A33	5.0	4.75	90.25	113	AlPO ₄ + AlPO ₄ (T) + L + V
A34	10.0	4.5	85.5	113	Augelite + L + V
A35	1.93	63.51	34.56	24	L + V
A36	3.86	65.42	30.72	57	L + V
A37	5.8	67.32	26.88	177	AP ₃ H ₆ + L + V
A38	7.73	69.23	23.04	177	AP ₃ H ₆ + L + V
A39	9.66	71.14	19.2	177	AP ₃ H ₆ + L + V
A45	1.0	1.98	97.02	394	AlPO ₄ + L + V
A46	2.0	1.96	96.04	399	AlPO ₄ (T) + L + V
A49	5.0	1.9	93.1	404	Augelite + L + V

Table II. (continued)

No.	Composition wt.-%			Time Hours	Phases present
	Al ₂ O ₃	P ₂ O ₅	H ₂ O		
A51	3.0	4.85	92.15	413	AlPO ₄ + L + V
A52	4.0	4.8	91.2	413	AlPO ₄ + L + V
A53	5.0	4.75	90.25	424	AlPO ₄ + AlPO ₄ (T) + L + V
A54	10.0	4.5	85.5	424	Augelite + L + V
A55	5.0	9.5	85.5	424	AlPO ₄ + L + V
A56	6.0	9.4	84.6	428	AlPO ₄ + L + V
A57	7.0	9.3	83.7	428	AlPO ₄ + L + V
A58	10.0	9.0	81.0	428	Augelite + AlPO ₄ (T) + L + V
A59	5.8	67.32	26.88	471	AP ₃ H ₆ + L + V
A60	6.18	67.71	26.11	590	AP ₃ H ₆ + L + V
A61	6.76	68.28	24.96	492	AP ₃ H ₆ + L + V
A62	7.73	69.23	23.04	590	AP ₃ H ₆ + L + V
A63	6.91	63.14	29.95	586	AlPO ₄ + L + V
A64	7.85	63.35	28.8	586	AlPO ₄ + L + V
A65	8.8	63.55	27.65	588	AlPO ₄ + L + V
A66	9.74	63.76	26.5	590	AlPO ₄ + L + V
A67	10.68	63.98	25.34	591	AlPO ₄ + L + V

Figure 1. Phase diagram of the system Al_2O_3 - P_2O_5 - H_2O at 200°C and 250 psi. Dashed lines on this isothermal isobaric section represent possible equilibrium relationships.

Figure 2. Phase relations at 200°C in the high H_2O region of the system Al_2O_3 - P_2O_5 - H_2O . The exact location of the isotherm at the corner was not determined and approaches pure water.

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III. The System $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$

The following is the second manuscript which will be submitted for publication in the Journal of the American Ceramic Society. This paper covers the results of the research conducted under this contract into the reactions at hydrothermal conditions of lime with the phosphoric acids.

There are three calcium phosphate hydrates which are stable at 200°C . They are hydroxylapatite, monetite and monocalcium orthophosphate monohydrate (MCPM). An acidic solution mixed with lime could set to form a cement bonded with MCPM but the reaction is so fast it could not be used in geothermal cementing. One of the methods currently being worked on in this investigation is retarding this reaction by bonding the calcium into a glass. The data will be used to design experimental cements. It will also be used in interpreting the results of the reactions in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ which are discussed below.

The System $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ at 200°C

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ABSTRACT

The phase diagram for the ternary system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ at 200°C and 250 psia was established. The solubility isotherm was determined by direct observation. Solid phases were analyzed by use of x-ray powder diffraction techniques and microscopy. Four solid phases were observed in equilibrium with liquid phases: Portlandite $\text{Ca}(\text{OH})_2$, hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, monetite CaHPO_4 and monocalcium orthophosphate monohydrate (MCPM) $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

I. INTRODUCTION

The system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ is important because of extensive use of calcium phosphates as commercial fertilizers. This investigation stems from work on phosphate cements. The equilibrium in this system has been studied by Elmore and Fair¹ at 25°C , 40°C , 50.7°C , 75°C and 100°C . They reported five solid phases in equilibrium with the phosphate solutions. They are hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and

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monetite CaHPO_4 ; monocalcium orthophosphate monohydrate (MOPM) $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ which is in equilibrium with the liquid of intermediate phosphoric acid concentration and monocalcium orthophosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in the high P_2O_5 region. The first three phases exist in equilibrium with solutions at the H_2O corner.

• Three ternary invariant points have been located in this system^{1,2,3}. The first one has been estimated to occur at 160°C with a liquid composition of 5.2% CaO and 54.5% P_2O_5 . At this point this liquid coexists with CaHPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Above this temperature, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ no longer exists in the system. The second invariant point corresponds to the equilibrium among CaHPO_4 , $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and the saturated solution of 0.05% CaO and 0.14% P_2O_5 at about 36°C . Above this temperature $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ disappears from the phase diagram. The third invariant point corresponds to the equilibrium among $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaHPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and the saturated solution at 20°C which is virtually pure water. Below this temperature CaHPO_4 no longer exists in equilibrium with a liquid phase.

II. EXPERIMENTAL PROCEDURE

The aqueous phosphate solutions with concentration of 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60% and 61.6% P_2O_5 were prepared from concentrated orthophosphoric acid (61.6% P_2O_5) by diluting with distilled water. Mixtures at different composition of $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ were prepared by mixing CaO or $\text{Ca}_3(\text{PO}_4)_2$ powder with the prepared phosphate solutions. The mixtures were charged

into heavy wall pyrex glass tubes (8mm OD, 5mm ID, 20 cm long) to about 3/5 capacity. Both ends of the glass tubes were sealed to secure a completely closed system. In all tubes a vapor exists after firing which is water saturated air. The pressure in the tube is calculated to be 250 psi (1700 kPa).

An oven set at 200°C was used for the isothermal chamber. The time required for the mixtures to reach equilibrium varies. A maximum of 26 days was given to certain compositions. Literature studies¹ suggested that equilibrium would be obtained in several days. After the system reached equilibrium, the glass tube was removed from the oven. An observation on whether the glass tube contained a clear solution or solutions and crystalline phases was made before the tube began to cool down. The solid phase in the sample was separated from the liquid immediately. This solid phase was ground and analyzed by x-ray diffraction technique. High temperature microscopy was used to identify some of the phases. Calcium concentration on some of the solutions was made by atomic absorption spectroscopy to check the liquidus isotherm determined by direct observation.

III. RESULTS AND DISCUSSION

Table I shows the results of 56 runs made for the determination of the 200°C solubility isotherm in the ternary system $\text{CaO} - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$. Three solid phases show their stability at this temperature, they are: hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, dicalcium orthophosphate or monetite, CaHPO_4 and monocalcium orthophosphate monohydrate $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. The solubility isotherm and the phase relations, as determined by these runs are shown

in Figure 1. Figure 2 showed a schematic location of the isotherm in the very high H_2O region of the system drawn on rectangular coordinates.

Hydroxylapatite is found as the solid phase in samples 20, 21, 22 and 23. No runs yielded hydroxylapatite, portlandite and a liquid. Therefore, the maximum solubility of CaO at the H_2O apex was not determined. At least 9 wt% CaO can be dissolved and small amounts of phosphate ion increase the solubility of lime.

Two solid phases, monetite and hydroxylapatite were found coexisting in sample 17 and 29. These two compositions must, therefore, lie in the three phase region where monetite and hydroxylapatite are two stable phases in equilibrium with a saturated liquid. All other samples shown in Figure 2 have the one solid phase, monetite, except 48 which is all liquid and therefore below the solubility limit.

Dicalcium orthophosphate, monetite, $CaHPO_4$ is the solid phase in equilibrium with the liquid over the range from the H_2O corner to about 50% P_2O_5 . This compound crystallized as triclinic tablets. The best region for the monetite crystallization is between 2% P_2O_5 and 20% P_2O_5 . In this region, the triclinic single crystal can grow to the size of 0.8mm in several days. The crystal size becomes small in the area where P_2O_5 is greater than 20%. In the high P_2O_5 region only a very fine powder of $CaHPO_4$ was obtained. The invariant liquid at high phosphate compositions which can coexist with monetite and monocalcium orthophosphate monohydrate (MCPM) falls at 6.5 wt% CaO : 50% P_2O_5 : 43.5% H_2O .

It is difficult to analyze accurately the solid phases and to locate the compatibility joins at 200°C in the high P_2O_5 region because of the fast reactions between monetite, MCPM and liquid phase when the sample is cooled down to room temperature. Monetite has a negative temperature coefficient of solubility, that is, the higher the temperature, the lower the solubility. So monetite will dissolve as temperature goes down. It was found that the rate of dissolution of monetite increases with the P_2O_5 concentration. Also, the smaller the monetite crystals, the higher the dissolution rate. Since the monetite crystals are large in the low P_2O_5 region, they do not dissolve when the sample is taken out of the oven, cooled down to room temperature and separated from the liquid phase. In sample 38, where the solid phase at 200°C is a very fine powder, all solid phase dissolved on cooling and the sample became a clear liquid in 10 minutes. This phenomenon also happened in samples 39, 31, 32, 42 and 4. X-ray diffraction analysis showed the presence of MCPM in these samples, this phase formed during cooling. The stable phase at 200°C observed by high temperature microscopy was monetite.

At temperatures above 160°C, MCPM has been reported to be unstable.¹ These observations were made in open systems which could lose water. In this research, MCPM was observed in samples 53, 54, 55 and 56 at 200°C. Because of difficulties in handling solutions and analyzing phases, no runs were made in the system at P_2O_5 compositions greater than 61 wt%. The liquidus isotherm must drop to the $H_2O - P_2O_5$ join at about 80 wt% P_2O_5 .

and will have to change direction drastically. This suggests that monocalcium orthophosphate (1·1·2) is stable at 200°C and would account for this change in the isotherm direction.

IV. CONCLUSIONS

The liquidus isotherm for the calcium phosphates extends from the H₂O corner to 6.5 CaO: 50 P₂O₅:43.5 H₂O and over this range monetite is the primary phase. At higher P₂O₅ concentrations Ca (H₂PO₄)₂·H₂O is encountered. A range of liquidus compositions from virtually pure water to at least 9% CaO with very low phosphate concentration are in equilibrium with hydroxylapatite.

Table I. Results of experiments made in the system

CaO - P₂O₅ - H₂O at 200°C.

No.	Composition wt.-%			Time days, hrs	Phases present
	CaO	P ₂ O ₅	H ₂ O		
C1	5.0	38.0	57.0	14d	L + V
C3	5.0	47.5	47.5	9d, 5h	L + V
C4	10.0	45.0	45.0	9d, 5h	Ca(H ₂ PO ₄) ₂ ·H ₂ O + L + V
C5	5.0	28.5	66.5	9d, 3h	CaHPO ₄ + L + V
C6	10.0	27.0	63.0	6d, 18h	CaHPO ₄ + L + V
C7	5.0	19.0	76.0	13d, 23h	CaHPO ₄ + L + V
C8	5.0	9.5	85.5	15d, 23h	CaHPO ₄ + L + V
C9	5.42	31.58	63.0	7d, 20h	CaHPO ₄ + L + V
C10	4.99	22.37	72.64	11d	CaHPO ₄ + L + V
C11	4.77	13.15	82.08	9d, 3h	CaHPO ₄ + L + V
C12	2.87	7.16	89.97	13d, 23h	CaHPO ₄ + L + V
C13	1.0	4.95	94.05	20d, 9h	CaHPO ₄ + L + V
C14	2.0	4.9	93.1	20d, 9h	CaHPO ₄ + L + V
C15	3.0	4.85	92.15	20d, 9h	CaHPO ₄ + L + V
C16	4.0	4.8	91.2	20d, 9h	CaHPO ₄ + L + V
C17	5.0	4.75	90.25	19d, 10h	CaHPO ₄ + Ca ₅ (PO ₄) ₃ OH + L + V
C18	1.0	1.98	97.02	11d, 4h	CaHPO ₄ + L + V
C19	2.0	1.96	96.04	15d, 4h	CaHPO ₄ + L + V
C20	3.0	1.94	95.06	16d, 20h	Ca ₅ (PO ₄) ₃ OH + L + V
C21	4.0	1.92	94.08	16d, 20h	Ca ₅ (PO ₄) ₃ OH + L + V

Table I. (continued)

No.	Composition wt.-%			Time days, hrs	Phases present
	CaO	P ₂ O ₅	H ₂ O		
C22	5.0	1.9	93.1	16d, 22h	Ca ₅ (PO ₄) ₃ OH+L+V
C23	10.0	1.8	88.2	12d, 19h	Ca ₅ (PO ₄) ₃ OH+L+V
C24	0.81	2.66	96.53	9d, 21h	CaHPO ₄ + L + V
C25	1.95	3.58	94.47	13d, 22h	CaHPO ₄ + L + V
C26	2.71	4.19	93.1	15d, 16h	CaHPO ₄ + L + V
C27	3.8	5.06	91.14	15d, 9h	CaHPO ₄ + L + V
C28	4.88	5.94	89.18	15d, 10h	CaHPO ₄ + L + V
C29	8.14	8.56	83.3	15d, 11h	CaHPO ₄ +Ca ₅ (PO ₄) ₃ OH + L + V
C30	4.88	40.52	54.6	5d	L + V
C31	5.97	40.63	53.4	13d, 5h	CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V
C32	7.05	40.75	52.2	13d, 20h	CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V
C34	1.0	29.7	69.3	9d, 12h	L + V
C35	2.0	29.4	68.6	9d, 12h	L + V
C36	3.0	29.1	67.9	9d, 12h	L + V
C37	4.0	28.8	67.2	9d, 12h	CaHPO ₄ + L + V
C38	6.0	37.6	56.4	26d, 2h	CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V
C39	7.0	37.2	55.8	26d, 2h	CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V

Table I. (continued)

No.	Composition wt.-%			Time days, hrs	Phases present
	CaO	P ₂ O ₅	H ₂ O		
C40	8.0	36.8	55.2	26d, 2h	CaHPO ₄ + L + V
C41	6.0	47.0	47.0	26d, 2h	L + V
C42	7.0	46.5	46.5	20d, 10h	CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V
C44	1.0	19.8	79.2	8d	L + V
C45	2.0	19.6	78.4	8d	L + V
C46	3.0	19.4	77.6	7d, 22h	CaHPO ₄ + L + V
C47	4.0	19.2	76.8	7d, 23h	CaHPO ₄ + L + V
C48	1.0	9.9	89.1	10d	L + V
C49	2.0	9.8	88.2	10d	CaHPO ₄ + L + V
C50	3.0	9.7	87.3	10d	CaHPO ₄ + L + V
C51	4.0	9.6	86.4	10d, 1h	CaHPO ₄ + L + V
C52	5.0	58.52	36.48	20d, 10h	L + V
C53	6.0	57.9	36.1	20d, 10h	Ca(H ₂ PO ₄) ₂ ·H ₂ O+L+V
C54	7.0	57.29	35.71	26d	Ca(H ₂ PO ₄) ₂ ·H ₂ O+L+V
C55	8.0	56.67	35.33	26d, 1h	Ca(H ₂ PO ₄) ₂ ·H ₂ O+L+V
C56	9.0	56.06	34.94	26d, 2h	Ca(H ₂ PO ₄) ₂ ·H ₂ O+L+V
C57	2.87	60.77	36.36	17d, 10h	L + V
C58	3.85	60.48	35.67	17d, 10h	L + V
C59	4.83	60.19	34.98	17d, 10h	L + V

Figure 1. The system $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ at 200°C and 250 psia .

Figure 2. Diagram of the high water region of the system CaO-P₂O₅-H₂O at 200°C showing a schematic location of the solubility isotherm.

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IV. The Reaction of Silicate Glasses with Phosphoric Acids

While phosphate cements have been used in well cementing in the past, an inability to control set time at elevated temperatures is one of the reasons for their lack of acceptance. Since one of the steps in the phosphate cementing reaction is the leaching of Ca^{++} and Al^{+++} from a glass phase we feel that by controlling that leach rate we can control the setting of phosphate cements. Toward the goal of controlling that leach rate a considerable effort has been made during the past quarter to understand the corrosion of silicate glasses by phosphoric acid.

The corrosion rate of a glass is related to the glass structure and chemistry. Pure SiO_2 when melted and solidified without crystallization to the glassy state resembles a three dimensionally cross-linked polymer. It is made up of somewhat tortuous chains of SiO_4 tetrahedral units linked to other SiO_4 units through common oxygen ions. This glass is extremely resistant to acid attack.

If CaO and Al_2O_3 are added to the silica in small amounts the larger and less highly charged ions bond into the glass structure. Instead of bonding to four oxygens as silicon does, Al^{+++} can bond to four or six oxygens and Ca^{++} can bond to eight, ten or twelve oxygens. The ion to oxygen bonds are far weaker and the ions are subject to replacement by a proton (H^+). However, if these ions are widely dispersed through a silica network while the surface ions may be leached (i.e. replaced by H^+)

no further attack takes place because bulk ion cannot diffuse through the silica network.

As the amount of Ca^{++} and Al^{+++} increase the continuous chains of silica get shorter and shorter, the structure becomes more open and the leaching rate increases. As the glass is depleted in ions, a silica layer which takes up water will be left behind as a silica gel layer. Such layers have been observed by other investigators.

As the CaO and Al_2O_3 content of the glass passes 50% of the total composition, the silica units become virtually isolated and unpolymerized or perhaps form dimer and trimer groups in the glass. Now the interaction of the glass with the acid can more properly be called dissolution. As the calcium and aluminum ions are dissolved the SiO_4 groups are also solubilized. All three of these behaviors have been observed in the calcium aluminum silicate glasses depending upon their composition and we have been able to relate the corrosion behavior to some cement forming behavior.

Thus far we have studied the corrosion of the following glasses: $30\text{CaO}:30\text{Al}_2\text{O}_3:40\text{SiO}_2$, $23.5\text{CaO}:23.5\text{Al}_2\text{O}_3:53\text{SiO}_2$, $22.5\text{CaO}:22.5\text{Al}_2\text{O}_3:55\text{SiO}_2$, $21.5\text{CaO}:21.5\text{Al}_2\text{O}_3:57\text{SiO}_2$ and $17.5\text{CaO}:17.5\text{Al}_2\text{O}_3:65\text{SiO}_2$. Each glass was melted and stirred and fibers were drawn from the melt. Sections of the fibers about an inch long were immersed in 30 percent phosphoric acid and the fibers were removed, dried and weighed to check weight loss. If the change in weight of the fiber was not greater than 0.0005 grams, it was ignored. Using the balance available we feel this is our lowest level of meaningful data.

Table I lists the data obtained at 90°C for the 40 wt% silica glass. There are three sets of data and they are plotted on Figure 1. A best fit curve has been drawn which yields a corrosion rate for the glass of 0.07 grams per cm² of surface area per hour. The figure indicates that absolute values are difficult to obtain and some statistical analysis of the data is necessary. This is not only true for this set of data, but it is true for all of our data and further discussion should be weighed with this important finding in mind.

The weight loss is linear with time. This indicates that no film is formed on the surface and no diffusion mechanisms are important to the attack. These tests are only run out to one hour because at the end of this period even the thickest fibers are totally dissolved. Runs were not made on this 40% glass at 140°C because the fibers would dissolve completely in minutes. At the lower temperatures, the fiber lasts for several hours before total dissolution. Table II lists the data obtained for this equal weight lime/alumina glass with 40% silica and Figure 2 shows the weight loss results. Again the loss appears to be linear. The rate is approximately 15 times slower than the rate at 90°C. Inspection under the microscope of these fibers shows no type of surface film after corrosion.

Table III lists the weight loss data on the 53 wt% SiO₂ and the 55 wt% SiO₂ at 40°C and 90°C. The remaining oxides in these two glasses are equal weights of CaO and Al₂O₃. Figures 3, 4 and 5 show weight loss curves for the 53% glass at 40°C and 90°C and the 55% glass at 90°C. No significant data was

Table I. Weight Loss Data For 40% Silica Glass

40 wt% SiO₂ Glass
90°C

30% H₃PO₄ Solution

Run 1

Sample: 1G₁₀⁹

Fiber No.	Time	Loss in Wt.(gms)	Surface Area (cm ²)	<u>Loss in Wt (gms)</u> <u>Surface Area (cm²)</u>
1G _{10,1} ⁹	10 mins.	0.0168	1.52	110.4 x 10 ⁻⁴
1G _{10,2} ⁹	20 mins.	0.0639	2.73	233.73 x 10 ⁻⁴
1G _{10,5} ⁹	5 mins.	0.0088	1.49	59.06 x 10 ⁻⁴
1G _{10,6} ⁹	15 mins.	0.0245	1.431	171.21 x 10 ⁻⁴
1G _{10,7} ⁹	2 1/2 mins.	0.0044	1.38	31.83 x 10 ⁻⁴
1G _{10,8} ⁹	7 1/2mins.	0.0129	1.795	71.89 x 10 ⁻⁴
1G _{10,9} ⁹	12 1/2 mins.	0.0134	1.30	103.3 x 10 ⁻⁴

40 wt% SiO₂ Glass

90°C

30% H₃PO₄ Solution

Run 2

Sample: 2G₁₀⁹

Fiber No.	Time	Loss in Wt.(gms)	Surface Area (cm ²)	<u>Loss in Wt.(gms)</u> Surface Area (cm
2G _{10,1} ⁹	2 1/2mins.	0.0093	1.54	60.34 x 10 ⁻⁴
2G _{10,2} ⁹	5 mins.	0.0031	0.596	52.04 x 10 ⁻⁴
2G _{10,3} ⁹	7 1/2 mins.	0.0169	2.49	67.83 x 10 ⁻⁴
2G _{10,4} ⁹	10 mins.	0.0216	1.78	121.49 x 10 ⁻⁴
2G _{10,5} ⁹	12 1/2 mins.	0.0169	1.45	116.86 x 10 ⁻⁴
2G _{10,6} ⁹	15 mins.	0.0170	1.28	132.35 x 10 ⁻⁴
2G _{10,7} ⁹	17 1/2mins.	0.0242	1.44	167.90 x 10 ⁻⁴
2G _{10,8} ⁹	20 mins.	0.0465	2.28	203.83 x 10 ⁻⁴

40 wt% SiO₂ Glass

90°C

30% H₃PO₄ Solution

Run 3

Sample: 3G₁₀⁹

Fiber No.	Time	Loss in Wt. (gms)	Surface Area (cm ²)	$\frac{\text{Loss in Wt. (gms)}}{\text{Surface Area (cm}^2\text{)}}$
3G _{10,1} ⁹	2 1/2 mins.	0.0044	1.105	39.82×10^{-4}
3G _{10,2} ⁹	5 mins.	0.0106	1.645	64.44×10^{-4}
3G _{10,3} ⁹	7 1/2 mins.	0.0109	1.336	81.62×10^{-4}
3G _{10,4} ⁹	10 mins.	0.0189	1.782	106.05×10^{-4}
3G _{10,5} ⁹	12 1/2 mins.	0.0138	0.915	150.82×10^{-4}
3G _{10,6} ⁹	15 mins.	0.0229	1.317	173.93×10^{-4}
3G _{10,7} ⁹	17 1/2 mins.	0.0369	1.856	198.84×10^{-4}
3G _{10,8} ⁹	20 mins.	0.0331	1.472	224.75×10^{-4}

$\frac{\text{Loss in Wt (gms)}}{\text{Surface Area (cm}^2\text{)}}$

Figure 1. Weight loss of glass fiber with time,
40 wt% SiO₂ glass, 90°C, 30 wt% H₃PO₄ solution.

Table II. Weight Loss Data For Silicate Glass Fibers

40 wt% SiO₂ Glass

40°C

30% H₃PO₄ Solution

Sample: G₁₀

Fiber No.	Time	Loss in Wt (gms)	Surface Area (cm ²)	<u>Loss in Wt (gms)</u> <u>Surface Area (cm²)</u>
G _{10,1}	10 mins.	0.0009	1.22	7.37 x 10 ⁻⁴
G _{10,2}	30 mins.	0.0038	1.44	26.4 x 10 ⁻⁴
G _{10,3}	1 hr.	0.0091	2.006	45.36 x 10 ⁻⁴
G _{10,7}	1 1/2 hrs.	0.0090	1.293	69.64 x 10 ⁻⁴
G _{10,4}	2 hrs.	0.0134	1.30	102.93 x 10 ⁻⁴
G _{10,9}	2 1/2 hrs.	0.0353	2.647	133.38 x 10 ⁻⁴
G _{10,11}	3 hrs.	0.0232	1.333	174.01 x 10 ⁻⁴
G _{10,12}	3 1/2 hrs.	0.0346	1.564	221.2 x 10 ⁻⁴
G _{10,5}	4 hrs.	0.0327	1.68	194.5 x 10 ⁻⁴

Figure 2. Weight loss vs time for the 40 wt% SiO₂ glass at 40°C in a 30 wt% H₃PO₄ solution.

Table III. Weight Loss Data On
Calcium Aluminosilicate Fiber

53 wt% SiO₂ Glass
40°C
30% H₃PO₄ Solution

Sample: G₉

Fiber No.	Time	Loss in Wt (gms)	Surface Area (cm ²)	<u>Loss in Wt (gms)</u> <u>Surface Area (cm²)</u>
G ₉₁	10 mins.	0*	1.114	0
G ₉₂	30 mins.	0.0002*	1.79	1.12 x 10 ⁻⁴
G ₉₃	1 hr.	0.0005*	1.65	3.03 x 10 ⁻⁴
G ₉₄	2 hrs.	0.0005*	2.03	2.46 x 10 ⁻⁴
G ₉₅	4 hrs.	0.0009	1.115	8.07 x 10 ⁻⁴
G ₉₆	8 hrs.	0.0024	1.226	19.58 x 10 ⁻⁴
G ₉₇	16 hrs.	0.0047	1.433	32.81 x 10 ⁻⁴
G ₉₈	32 hrs.	0.0112	2.085	53.72 x 10 ⁻⁴
G ₉₉	64 hrs.	0.0192	1.953	98.32 x 10 ⁻⁴
G ₉₁₀	128 hrs.	0.0237	1.552	152.71 x 10 ⁻⁴

* Loss below level of significance.

Table III. (continued)

53 wt% SiO₂ Glass

90°C

30% H₃PO₄ SolutionSample G₉⁹

Fiber No.	Time	Loss in Wt (gms)	Surface Area (cm ²)	<u>Loss in Wt (gms)</u> <u>Surface Area (cm²)</u>
G ₉₁ ⁹	10 mins.	0	1.0684	0
G ₉₂ ⁹	30 mins.	0.0005*	1.307	3.83 x 10 ⁻⁴
G ₉₃ ⁹	1 hr.	0.0023	1.252	18.37 x 10 ⁻⁴
G ₉₄ ⁹	2 hrs.	0.0093	1.725	53.91 x 10 ⁻⁴
G ₉₅ ⁹	4 hrs.	0.0136	1.477	92.08 x 10 ⁻⁴
G ₉₆ ⁹	8 hrs.	0.0271	1.78	152.25 x 10 ⁻⁴
G ₉₇ ⁹	16 hrs.	0.0515	2.606	197.63 x 10 ⁻⁴
G ₉₈ ⁹	32 hrs.	0.0404	2.156	187.35 x 10 ⁻⁴
G ₉₉ ⁹	64 hrs.	0.0402	2.432	165.3 x 10 ⁻⁴
G ₉₁₀ ⁹	128 hrs.	0.0516	2.655	194.35 x 10 ⁻⁴

* Loss below level of significance.

Table III. (continued)

55 wt% SiO_2 Glass
40°C
30% H_3PO_4 Solution

Sample: G_6

Fiber No.	Time	Loss in Wt (gms)	Surface Area (cm^2)	<u>Loss in Wt (gms)</u> <u>Surface Area (cm^2)</u>
G_{61}	10 mins.	0.0004*	2.24	1.79×10^{-4}
G_{62}	30 mins.	0.0004*	1.73	2.31×10^{-4}
G_{63}	1 hr.	0.0003*	1.36	2.21×10^{-4}
G_{64}	2 hrs.	0.0004*	2.16	1.85×10^{-4}
G_{65}	4 hrs.	0.0001*	1.94	0.52×10^{-4}
G_{66}	8 hrs.	0.0001*	1.81	0.55×10^{-4}
G_{67}	16 hrs.	0.0002*	1.55	1.29×10^{-4}
G_{68}	32 hrs.	0.0001*	2.471	0.41×10^{-4}
G_{69}	64 hrs.	0.0001*	2.17	0.461×10^{-4}
G_{610}	128 hrs.	0.0002*	3.57	0.56×10^{-4}

* Loss below level of significance.

Table III. (continued)

55 wt% SiO₂ Glass
 90°C
 30% H₃PO₄ Solution
 Sample: G₆⁹

Fiber No.	Time	Loss in Wt (gms)	Surface Area (cm ²)	<u>Loss in Wt (gms)</u> <u>Surface Area (cm²)</u>
G ₆₃ ⁹	1 hr.	0*	2.413	0
G ₆₄ ⁹	2 hrs.	0.000*	1.414	0.707 x10 ⁻⁴
G ₆₅ ⁹	4 hrs.	0*	2.283	0
G ₆₆ ⁹	8 hrs.	0.0001*	2.77	0.36 x10 ⁻⁴
G ₆₇ ⁹	16 hrs.	0.0001*	2.87	0.35 x10 ⁻⁴
G ₆₈ ⁹	32 hrs.	0.0004*	2.706	1.48 x10 ⁻⁴
G ₆₉ ⁹	64 hrs.	0.0008	3.243	2.47 x10 ⁻⁴
G ₆₁₀ ⁹	128 hrs.	0.0017	3.69	4.60 x10 ⁻⁴

* Loss below level of significance.

Figure 3. Weight loss results for 53 wt% SiO₂ glass at 40°C in 30 wt% H₃PO₄ solution.

Figure 4. Weight loss data for 53 wt% SiO₂ glass
at 90°C in 30 wt% H₃PO₄ solution.

Figure 5. Weight loss data for 55 wt% SiO₂ glass
at 90°C in 30 wt% H₃PO₄ solution.

obtained for the 55% glass at 40°C and the weight losses of the fibers are below our level of detection. Corrosion rates have been taken from these data and will be discussed below. In the last quarterly report, corrosion data was reported for the 55% glass, the 57% glass and the 65% glass. The experiments on 65% do not show a detectable loss of weight. The 57% glasses fall in the same category.

From the above data, best fit curves have been drawn and the slopes of those curves have been measured to give the corrosion rates of the glasses at the various temperatures. These data are listed in Table IV and the data is plotted on Figure 6. The precipitous rise that occurs above a given silica content, separates the insoluble glasses from the soluble glasses. The change takes place over a very small range of silica content.

This finding is of basic importance to the phosphate cement program. No glass in this series higher in silica than 54% will form a cement at room temperature or at 90°C because there is no interaction of the liquid with the frit powder. The cementing interactions of the other glasses with the liquids will be discussed below. The effect of temperature on the corrosion rate can be seen by comparing the rates in the Table IV. This effect is considerable and its importance to cement formation for geothermal purposes is also discussed below.

Between the extremely soluble glasses and the insoluble glasses there is a composition that shows unique corrosion behavior. Associated with the corrosion is the formation of a silica rich film which grows in thickness as Ca^{++} and Al^{+++} is leached from the glass. Figure 7 shows two micrographs of the

TABLE IV. Corrosion Rate Of The
Calcium Aluminosilicate Glasses

Temperature = 40°C

% SiO ₂ in Glass	<u>Loss in Wt (gm)</u>
	<u>Surface Area (cm²)</u> Hr.
40	49.5 x 10 ⁻⁴
53	1.375 x 10 ⁻⁴
55	Below level of detection
57	Below the level of detection
65	Below the level of detection

Temperature = 90°C

% SiO ₂ in Glass	<u>Loss in Wt (gm)</u>
	<u>Surface Area (cm²)</u> Hr.
40	701.2 x 10 ⁻⁴
53	12.35 x 10 ⁻⁴
55	0.036 x 10 ⁻⁴
57	Below the level of detection
65	Below the level of detection

Figure 6. Corrosion rate of glass fibers as a function of silica content.

silica film on the fiber. Both of these are formed on the 53% SiO_2 glass at 40°C . The film remaining is a silica gel phase. Chemical analysis shows considerable enrichment of the SiO_2 and depletion of calcium and aluminum. The index of refraction of the glass is 1.57. The index of refraction of the film phase is 1.415 which indicates only silica and water are present in the gel. Calcium and aluminum would raise the index of refraction. Also, our chemical analysis shows only a trace of phosphorous in the gel phase. Upon removal of the fiber from the leaching phosphoric acid, the film is not visible. On drying, the shrinkage of the gel due to loss of water produces cracks which scatter light and make the phase visible as a white coating on the fiber. Calcium and aluminum ion must be exchanged for hydrogen ions and water is adsorbed in the film. This adsorption produces an increase in volume of the fiber.

Examination of Figure 4 shows that initially the glass loses weight as calcium and aluminum are leached from the glass. Accompanying the weight loss is a growth in the film layer. After 16 hours, there is no glass remaining. The entire fiber has been replaced with the silica gel phase. Continued immersion in phosphoric acid does not change the weight of the silica gel phase. The conclusion is that no interaction of phosphate and the silica gel takes place and that there are probably no silicophosphate phases in a glass bonded phosphate cement. Furthermore, Figure 4 indicates that the initial weight loss is linear. Previous investigators have shown that surface films cause corrosion rates to be parabolic with corrosion

Figure 7(A). G910 (128 hrs, 40°C, 53% SiO₂ glass). The fiber has deteriorated to a very great extent. The unattacked fiber and the film formed on it are clearly visible. The thickness of the unreacted fiber is measured. It is 0.2 mm. The thickness of the fiber with the film is 1.8 ± 0.1 mm. The average thickness of the fiber before immersing it in acid is 1.235 mm. Thus an increase in fiber thickness has taken place.

Figure 7(B). The 53% SiO₂ glass fiber, G99 after 64 hrs. at 40°C. The thickness of the unattacked fiber is 1 mm.

being controlled by the rate at which ions diffuse through the film. If the linear relationship shown here is correct then diffusion through the film must not be rate controlling.

The work on these effects will continue and plans for presenting some of this work at the fall meeting of the glass division of the American Ceramic Society are underway.

V. The Quaternary System: $\text{CaO}:\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:\text{H}_2\text{O}$

That cements can be made from silicate glasses from which Ca^{++} and Al^{+++} is leached and react with phosphoric acid is established in the next section. The cementing phase is probably a calcium aluminophosphate hydrate. Preliminary work has shown that at 200°C the phase, crandallite, $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ which has an alunite structure is one of the stable phases. Other stable phases in the system must be identified so that cements can be designed to make use of that phases which will be stable under geothermal conditions.

Toward this end, and using the sealed pyrex tube method a more thorough investigation of this ternary is underway. Figure 8 shows the ternary system. Three solid mixtures are used: the 25% CaO , the 50% CaO and the 75% CaO . In each tube there is a 90 liq: 10 solid mixture which is brought to equilibrium. The liquids used are 10% P_2O_5 phosphoric acid to 50% phosphoric acid. About 60 tubes have been sealed. They are now being held in the ovens to reach equilibrium. They will be opened and analyzed by x-ray diffraction during the next quarter.

Figure 8. The system $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ showing the compositions under investigation at 200°C .

VI. CEMENT TESTING

Testing of two series of compositions have begun. The goal is to determine if these compositions form cements when mixed with phosphate solutions, what their setting time is and if they are insoluble. The two series of compositions are the calcium aluminum silicate glasses and pure alumina.

Table 5 lists the cementing characteristics of the calcium aluminum silicate glasses on which we also have solubility data. Cements with the pure glass and alumina as a filler were made using 30% H_3PO_4 and 40% H_3PO_4 saturated with dissolved aluminum oxide. The results show that only the 40% SiO_2 and 53% SiO_2 glass frits have cementing properties. As seen in the report above these two glasses are the only two with measurable solubilities. As proposed then our understanding of glass solubilities will aid greatly in the design of geothermal cements.

Referring to Figure 9 , a set of solubility curves are drawn for the glasses based on the preliminary findings presented above. Any glass composition, at a given temperature which falls to the right of the solubility rise will be virtually insoluble and will not form a cement. A composition to the left of the rise will set rapidly as a phosphate cement. A composition falling at point A would be insoluble in phosphoric acid at room temperature. The composition could be mixed with acid and held indefinitely as a plastic mass. If the geothermal cementing zone is 200°C the cement could be pumped into place and only then would setting begin as the phosphoric acid dissolved the

TABLE V.
Cementing Characteristics
of
Silicate Glasses

Temperature = 20-25°C

Powder Used	Liquid Added	Setting Characteristics
1. 40 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Setting time is 1 min.
2. 40 wt% SiO ₂ glass	Al ₂ O ₃ buffered phosphate solution	Sets in 1 hour.
3. 2:1 by wt mixture of Al ₂ O ₃ powder and 40 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Sets in 1 hour
4. 53 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Takes 1 hour to set but breaks on touching
5. 53 wt% SiO ₂ glass	Al ₂ O ₃ buffered phosphate solution	Does not set after 2 1/2 days
6. 2:1 by wt mixture of Al ₂ O ₃ powder and 53 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Does not set after 2 1/2 days
7. 55 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Does not set after 1 day.
8. 55 wt% SiO ₂ glass	Al ₂ O ₃ buffered phosphate solution	Does not set after 1 day
9. 2:1 by wt mixture of Al ₂ O ₃ powder and 53 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Does not set after 1 day
10. 57 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Does not set after 1 day
11. 57 wt% SiO ₂ glass	Al ₂ O ₃ buffered phosphate solution	Does not set after 1 day
12. 2:1 by wt mixture of Al ₂ O ₃ powder and 57 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Does not set after 1 day

TABLE V.
(continued)

Powder Used	Liquid Added	Setting Characteristics
13. 65 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Does not set after 1 day
14. 65 wt% SiO ₂ glass	Al ₂ O ₃ buffered phosphate solution	Does not set after 1 day
15. 2:1 by wt mixture of Al ₂ O ₃ powder and 65 wt% SiO ₂ glass	30 wt% H ₃ PO ₄ solution	Does not set after 1 day

Figure 9. Hypothetical solubility curves for calcium aluminum silicate glasses at various temperatures.

glass and the cementing phases began to form. We will continue to obtain solubility data on this system to see if the model shown in Figure 9 is correct.

The discovery of augellite, $\text{Al}_2\text{PO}_4(\text{OH})_3$, as a stable hydrate at 200°C suggests a cement can be made up of γ -alumina and 60% P_2O_5 phosphoric acid. If the cement is pumped into place and held at 200°C , the following reactions which could be cement producing would take place:

1. The liquid becomes saturated in aluminum ion by the dissolution of Al_2O_3 . This would produce a viscous plastic mass.

2. As more alumina entered the liquid phase, berlinite crystals would begin to form cementing together the grains of alumina still not dissolved. As this took place, the pH of the solution would begin to rise as the liquid composition shifted toward water.

3. The cement which began as roughly 50% liquid (acid) and 50% γ -alumina would now contain about 15% of a liquid phase which would be essentially water. This "water" would dissolve Al_2O_3 and react with berlinite to result in a solid mass of augellite. A filler could be added to cut down volume shrinkage if this were a problem. The experiments on these cements are underway and the results will be included in the next quarterly report.

VII. FUTURE WORK

As described in the various sections above work will continue during the next quarter on the following areas:

1. With the work completed on the systems $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ a study will be undertaken to determine the stable phases at 200°C in the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$.

2. The study of the solubility of the calcium aluminum silicate glasses will continue to determine the solubility rates as a function of temperature, phosphate liquid composition and percent of silica.

3. Cementing characteristics of the calcium aluminum silicates will be determined and correlated with the findings on solubility.

4. Physical property data on the best cements will be obtained as the optimum compositions are identified.

C00/4190-3

DEVELOPMENT OF GEOTHERMAL WELL COMPLETION SYSTEMS

PHASE II: Progress Report No. 2
April - June, 1978

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Executive Summary

Phase II of Dowell's DOE contract has continued this quarter with work on the development of a new and improved geothermal cementing system as well as continued effort to build a database of information on systems already in use. After establishment of initial test criteria through geothermal operator surveys, a screening program is well underway to determine the best potential candidates for more rigorous portions of the testing program.

Based on the preliminary results of this screening program, several cementing systems showing promise as potential geothermal cements have been moved into static brine exposure tests to determine their stability under hostile conditions of temperature and chemical environment. In this static testing program cement samples are exposed to synthetic brine prepared to simulate conditions actually encountered in a geothermal well. Early indications are that most Portland-based systems fare quite well in light brines but that severe degradation occurs in many cases when the cements are exposed to heavier brine solutions. The most stable systems in heavy brines appear to be those containing 35 to 40 percent silica flour (less than 200 mesh). Other silica of a coarser nature does not provide adequate stabilization of Portland systems under heavy brine exposure.

The static tests mentioned above serve as a precursor to more rigorous dynamic brine exposure tests currently in the planning and equipment preparation stages. Dynamic testing will be conducted both in the lab using a geothermal simulator and in the field using actual flowing geothermal wells located at the East Mesa Test Facility and at the San Diego Gas and Electric Company's facility in southern California. The simulator has

been designed by Dowell's chemical and process engineering group and all parts and equipment ordered. It should be on-line by the end of September, 1978.

Chemical studies have centered on the preparation and evaluation of scawtite as a chemical binder in Portland cement due to its chemical similarity to xonotlite, a known binder of high strength characteristics. Initial efforts show that a high concentration of scawtite results in a Portland system when 10 to 25 percent sodium bicarbonate is added to the mix and that compressive strength appears to correlate with scawtite concentration in a positive fashion.

Further work on a blend of furfuryl alcohol and powdered coal as a non-Portland alternative has continued with emphasis on controlling the large exotherm which results upon polymerization of the alcohol with an acid catalyst. Use of a partially polymerized starting material has reduced the problem considerably and made it possible to measure thickening times for the system.

INTRODUCTION

Phase II of Dowell's contract with the Department of Energy is well underway with work continuing in the areas of (1) Placement measurements, (2) stability measurements, (3) chemical studies and (4) development of non-Portland systems. Much of the work reported this quarter lies in the area of stability measurements, but some discussion of the other areas will be included.

INITIAL SCREENING PROGRAM

The initial screening program as described in report number COO/4190-1¹ is progressing and is currently centered on the areas of compressive strength and permeability testing. Most of the thickening time data has already been reported² and the most promising systems moved on to further screening. Table 1 presents a compilation of the compressive strength data collected to date. These tests were run for seven days and indicate that several systems are falling below the suggested minimum value of 1000 psi at seven days.¹ This portion of the program is continuing with samples cured at 1, 3, and 28 day intervals still to be evaluated. The three day samples will also be utilized in obtaining permeability data. These will be core drilled as 1 inch cylinders and placed in "Ruska" cells for determination of their permeability to a 3 percent brine solution.

STABILITY MEASUREMENTS - Brine Exposure Testing

Cement systems that appear to be potentially suitable for use in geothermal wells will be tested for stability when exposed to corrosive brines at high temperatures. Testing will be performed under both static and dynamic conditions in brines selected to be representative of those encountered in actual well conditions.

Table 2 shows the brines which will be employed in our testing program. The heavy and light synthetic brines are planned for both static and dynamic laboratory exposure tests while the natural "Nilands" brine will be used in field tests conducted at the San Diego Gas and Electric Company's facilities at Nilands, California.⁶ Recipes for the preparation of the synthetic brines are given in Table 3. The composition of both these brines are based on data collected and tabulated by Cosner and Apps.³

The "Salton Sea" brine is an average of approximately eighty analyses of various brines from the Imperial Valley as reported by these authors. Figure 1 shows a graphical representation of the concentration distribution of the various species present. The solid black line represents the arithmetic mean in each case. Concentrations of the Nilands natural brine components have been indicated with broken lines as a point of comparison.

The "East Mesa" brine, on the other hand, is from a single analysis considered to be most reliable by Apps⁴ and is probably more representative of brines encountered in 90 to 95 percent of the KGRA's⁵ than is the more highly concentrated "Salton Sea" version. This particular light brine will be the medium used in the majority of our dynamic brine exposure testing, both in our laboratory and at the East Mesa test facility in southern California.

Static Testing

A number of preliminary static tests have been conducted in both the light ("East Mesa") and heavy ("Salton Sea") brines on selected cement systems for seven and 28 days. These tests are a precursor to the selection of candidates for the more rigorous dynamic testing to be described later in this report. Samples were cured for 24 hours in fresh water at 150°C before

exposure to test conditions. Results of these tests as well as effect of exposure to dry heat are given in Tables 4 through 6. X-ray diffraction studies of selected systems are reported in Table 7.

The tests in light brine solution gave results about as expected from previous experience with fresh water tests.⁷ There is, however, some indication that under these conditions medium-size silica (70 to 200 mesh) is not producing the degree of Portland stabilization afforded by silica flour (smaller than 200 mesh). A few very light weight systems are also showing signs of deterioration. In other systems where the calcium to silica (C:S) ratio was about one to one, the original tobermorite produced at 150°C⁷ slowly converted to xonotlite with traces of other compounds.

In heavy brine, many lightweight systems performed quite differently than expected in that the various compositions did not convert to similar products upon exposure. For example, a Class G cement containing bentonite and perlite converted to xonotlite with normal strengths if stabilized with silica flour (Table 4, No. G6). The same system, however, when stabilized with medium silica, converted to the much weaker and more highly permeable kilchoanite and C_8S_5 type compounds (Table 4, No. G17). Other systems converting to weak and permeable phases after exposure to heavy brine include: Class "J" with bentonite/perlite (Table 4, No. J3); lime-silica with bentonite/perlite (Table 4, No. L2); and Class "J" with bentonite alone (Table 4, No. J5). It should be noted that these results are for duplicate runs of a single mix of cement and should therefore be considered preliminary until they can be confirmed with further experiments.

In addition to the tests discussed above, several types of specialty cements were evaluated including slag cements, aluminous cements, phosphate cements, and a furfuryl alcohol/

coal blend. The slags compared fairly well to the calcium silicate cements but offer no particular advantage over these. Aluminous cements fared rather poorly while the aluminum phosphate cement showed low strength but acceptable permeabilities, especially in heavy brine solutions. The furfuryl alcohol/coal systems had excellent strength and permeability when exposed to the high temperature brines but became charred and highly permeable under conditions of dry heat.

It should be mentioned that, generally speaking, most of the samples stood up better under dry heat than under brine exposure conditions. Strengths were excellent, and, when the samples were re-wetted, water permeabilities were low. The one noticeable exception to this was Class "J" cement with fly ash which became very weak when heated dry. Some of the samples developed surface cracks when re-wetted and have been noted in the Tables.

In order to test the effect of formation materials upon cement integrity, several of these materials were admixed with a Class G cement stabilized with silica flour. These mixtures were then allowed to set and cured under the same conditions used in the static brine stability tests discussed above. Table 8 shows the exact compositions of the test samples as well as the effects of sandstone, limestone, hardened clay, shales, feldspars, graywacke, tuff, serpentine, and granite upon compressive strength and permeability. Of all the materials checked, only the clay sample appeared to have a deleterious effect upon the cement systems under study. This particular sample (Table 7, No. F3) was considerably weaker and more permeable, probably due to the increased amount of mix water necessary to prepare the slurry.

Dynamic Testing

As mentioned earlier in this report, dynamic brine exposure testing will be carried out, both in the laboratory and in

the field. Laboratory testing will be conducted in a geothermal simulator which has been dubbed the Dynamic Brine Exposure Testing Apparatus or D-BETA for short. A sketch of the D-BETA is shown in Figure 2. This will be a recirculating system in which the brine at temperatures up to 350°C flows past the face of cylindrical sample plugs at a controlled rate for a specified period of time. Samples will subsequently be removed and examined in a series of tests including visual examination, compressive strength measurement, permeability measurement, x-ray diffraction and SEM analysis, etc. Baseline operation conditions were ironed out in a meeting at DOE's Washington offices on May 4, 1978, and are as follows: (1) cell temperature, 325°C, (2) cell pressure, 2200 psi and (3) brine composition, East Mesa synthetic as given in Table 3 of this report.⁸

Under these extreme conditions of temperature and corrosiveness, material of construction has been of prime consideration. Based upon limited data available from the literature⁹⁻¹⁴, autoclave corrosion tests were performed upon the most promising metal alloys for Dowell by Huntington Alloys, Huntington, West Virginia. Table 9 shows the results of corrosion testing upon Monel 400, Inconel 600, Inconel 625, and 1020 steel as a control. Based on this data, cost factors, and ready availability, Inconel 600 was chosen as the construction material. All necessary parts and equipment for construction of the D-BETA have been ordered and should be in hand before the end of the third quarter, 1978.

Dynamic field testing is scheduled to begin in September or October at two locations: (1) East Mesa Test Facility near El Centro, California, and (2) San Diego Gas and Electric Company's Facility near Nilands, California.

A formal request has been placed to A. J. Adduci at the San Francisco Operations Office of the Department of Energy for

permission to test at the East Mesa anomaly. A less formal request and explanation of our proposed test apparatus has been sent to Ken L. Newman of Westec Services, Inc. Ken will be directly helping us set up for testing at East Mesa. At East Mesa, well 6-1 will be used for testing in a test apparatus very similar to the simulator described above. All pressure vessels must be rated for 300 psi or greater and all equipment must meet current OSHA requirements. The plumbing of the apparatus, directly into the flowing brine pipeline, will be performed by Westec Service, Inc. personnel. The personnel at East Mesa are extremely cooperative and willing to work with us if we need their assistance.

The Niland facility is located geographically very close to East Mesa. At the Niland facility there is only one method which is feasible for sample testing. The proposed test procedure is to place the set samples inside a wire cage and fasten this cage inside of any of the flashers. In any case, this method should be very practical since heat up and cool down of their system is very slow and thus thermal shock should not be a problem, but the sample will be subjected to as harsh an environment as possible because there should be steam, liquid, and turbulent action during flashing. If cement samples can withstand this intense environment it should be a good indication of their utility. The facility shuts down at approximately 1000 hours intervals and during those intervals our sample could be removed and inspected.

Chemical Studies

One of the phases often encountered in cements cured at elevated temperatures is scawtite. The chemical formula for this compound is $\text{Ca}_{7/6} \text{Si}_{6/21} \text{O}_{16} \cdot \text{CO}_3$ and it is denoted in the shorthand of the cement chemist as $\bar{\text{C}}_7 \text{S}_{16} \text{CH}_3$. Scawtite is usually formed when carbon dioxide is present as an impurity as the cement sets.¹⁵ Since the phase is chemically quite similar to

xonotlite, a compound often observed in Portland cements used in geothermal applications and associated with medium to high compressive strengths, scawtite has a good chance of being a superior binder and merits investigation. In addition, since it is stable at both 230 and 315°C, it could prove useful over a wide range of geothermal cementing temperatures.

Several formulations of Portland cement, silica, and various carbonates were tried at different temperatures in an effort to successfully synthesize scawtite in reasonable quantities. Exact formulations used and results of the work are shown in Tables 10 and 11. Discussion of results follows.

Scawtite was successfully prepared at 232°C and 3000 psi curing pressure by the addition of calcium carbonate, sodium carbonate, and sodium bicarbonate to slurries containing 35% silica by weight of cement. Initial tests contained amounts of carbonate varying from 1 to 10 percent by weight of cement. In all of these initial tests only minor amounts (10-30%) of scawtite were formed, however, a trend was noticed that as scawtite concentration increased, so did compressive strength. As expected, another trend was noted in that the amount of scawtite formed appeared to directly proportional to the amount of carbonate added. On this basis, additions of 10, 25, and 50 percent bicarbonate by weight of cement were added to slurries containing 35% silica and cured for three days at 232°C and 3000 psi. The 10 and 25 percent slurries showed the major constituent to be scawtite. The 10% bicarbonate sample was very crystalline and consequently exhibited poorer strength than the less crystalline 25% sample. Based on these results, a quantity of 15% carbonate addition has been chosen as optimum and any further testing will be done at this concentration level.

In summary, scawtite can be formed at 232°C and it is showing signs of being a good binder. Due to relatively unsuccessful

attempts to prepare scawtite at 149 and 316°C, more extensive testing will be required at these temperatures to include higher carbonate concentrations and longer curing times. Further work will also involve a more detailed study of the physical properties of scawtite such as compressive strength, permeability and volume changes.

NON-PORTLAND SYSTEMS - Furfuryl Alcohol/Coal Blends

During initial testing of furfuryl alcohol polymers as possible cemental materials it was determined that the set polymer gave exceptionally good strength at very low density.² However, an extreme exotherm takes place when the alcohol polymerizes. The exotherm was of such a violent nature that obtaining thickening time data on systems containing only furfuryl alcohol and catalyst was halted.

Presently a 50:50 mixture by volume of furfuryl alcohol and a partially polymerized furfuryl alcohol solution is being evaluated. The partially polymerized resin is produced by Quaker Oats and named experimental resin 4607. The exact laboratory blend is 250 mls of furfuryl alcohol plus 250 mls of experimental resin 4607 plus 300 grams of < 20 mesh coal plus catalyst. Current testing is using ZnCl_2 as the catalyst. The ZnCl_2 is prepared in a 50% weight by volume solution, i.e., 50 grams ZnCl_2 added to 50 mls of water. A particular range of between 1 ml and 5 mls of ZnCl_2 solution will give a thickening time between 1 and 6 hours. This system still gives a violent exotherm but the pressure increase which was uncontrollable during our initial testing is now controllable. A thickening time of approximately 5 hours is desirable.

Exact formulations for proper thickening times will be determined and the extent of each exotherm closely monitored. Upon completion of thickening time data a more comprehensive evaluation of suitable systems can be undertaken.

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Figure 1. Distributions of concentrations of Salton Sea Brines. Data from Cosner and Apps.³ Solid lines represent arithmetic mean -- broken lines show concentrations of "Nilands" brine from Table 2.

Figure 2. Dynamic brine exposure testing apparatus (D-BETA).

TABLE 1

Results of compressive strength screening program completed to date. Samples were cured for seven days under 3000 psi pressure at the specified temperatures. Additive codes are given at the end of Table 4.

Cement	Additives (Percent by weight of Cement)								% Water	Comp. Str.(psi)	
	Code	Amt.	Code	Amt.	Code	Amt.	Code	Amt.		227°C	316°C
Permanente "G"	Sand	35	R1	1.0					34	5410	6887
	SF	35	R1	1.0					54	7113	4550
	SF	35	R1	1.0	FA	79			52	6013	1437
	SF	35	R1	1.0	PERL	8.5	BENT	2	116	1412	1068
	SF	35	R1	0.8	NaCl	20			54	4518	4869
	SF	35	R1	1.0	NaCl	5.4			54	2975	5277
	SF	35	R1	1.0	KCl	20			54	6169	3894
	SF	35	R1	1.0	KCl	5.4			54	6850	--
	SF	35	R1	1.0	DE	8.86			91.2	2131	1921
	SF	35	R1	1.0	COAL	27			63	3137	1415
	SF	35	R1	1.0	ILLM	27			63	2375	762
	SF	20	R1	1.0	DE	20			125	1569	641
	SF	35	R1	1.0	NaCl	6.8	BENT	16	135	847	547
Ideal "B"	SF	35	R1	1.5					56	5856	2731
	SF	35	R1	0.6	PERL	8.5	BENT	2	118	1526	884

TABLE 2

Brines selected for exposure testing of candidate cement systems. "Recipes" for synthetic brines are given in Table 3.

Species	Concentration (milligrams per liter)		
	Heavy(Salton Sea Avg. Syn.)	Heavy(Nilands Nat.)	Light(East Mesa Syn.)
Na	49,700	47,100	8,100
Ca	26,400	22,700	1,360
K	15,130	12,000	1,050
Fe	1,485	240	9
Mn	1,176	625	--
Ba	260	140	14
Sr	520	--	320
Zn	564	160	--
Li	224	--	40
B	370	--	10
Pb	95	29	--
Mg	480	165	17
Al	193	--	--
Cu	--	0.6	--
NH ₄	365	--	41
Cl	145,500	131,200	15,850
Br	104	--	--
CO ₂ *	610	--	200
SO ₄	84	--	43
TDS (Calc.)	243,300	214,400	27,050

* Note: CO₂ figures include carbonate in all forms.

TABLE 3

"Recipes" for synthetic brines listed in Table 2. Solutions A and B are mixed together in each case to prepare three liters of brine.

Component	Amount Added For Specified Brine	
	Heavy (Salton Sea Avg. Syn.)	Light (East Mesa Syn.)
Solution A:		
Water	2000 ml	1985 ml
NaCl	373.5 g	61.0 g
CaCl ₂	219.6 g	11.3 g
KCl	86.4 g	6.0 g
SrCl ₂ · 6H ₂ O	4.74 g	2.30 g
NH ₄ Cl	3.24 g	0.40 g
LiCl	4.11 g	0.70 g
MgCl ₂ · 6H ₂ O	17.73 g	0.30 g
BaCl ₂ · 2H ₂ O	1.05 g	0.07 g
PbCl ₂	0.39 g	----
MnCl ₂ · 4H ₂ O	21.6 g	----
ZnCl ₂ (97%)	3.60 g	----
FeCl ₂	10.11 g	----
AlCl ₃ · 6H ₂ O	5.01 g	----
Solution B:		
Water	960 ml	1000 ml
FeSO ₄ · 7H ₂ O	---	0.13 g
Al ₂ (SO ₄) ₃ · 18H ₂ O	0.60 g	---
Na ₂ SO ₄	---	0.12 g
H ₃ BO ₃	6.36 g	0.19 g
NaHCO ₃	3.48 g	0.83 g
NaBr	0.39 g	---

TABLE 4

Systems evaluated in static brine exposure testing program. Additive codes are given at the end of the table.

No.	Cement	- ADDITIVES (Percent by Weight of Cement) -								% Water	Weight (lb/gal)
		Code	Amt.	Code	Amt.	Code	Amt.	Code	Amt.		
G1	Permanente "G"	R1	0.8	SAND	35					54	15.9
G2		R1	0.8	SAND	50					58	16.0
G3		R1	0.8	SF	35					54	15.9
G4		R1	0.8	SF	50					58	16.0
G5		R1	0.7	SF	35	FA	79			93	15.1
G6		R1	0.6	SF	35	BENT	2	PERL	9	113	13.5
G7		R1	0.6	SF	35	NaCl	20			54	16.1
G8		R1	0.8	SF	35	NaCl	5.4			54	16.0
G9		R1	0.6	SF	35	KCl	20			54	16.1
G10		R1	0.8	SF	35	KCl	5.4			54	16.0
G11		R1	0.8	SF	35	DE	9			91	14.5
G12		R1	0.7	SF	35	COAL	25			63	14.6
G13		R1	0.7	SF	35	GILS	25			63	14.5
G14		R1	0.7	SF	35	SSS	2.5			122	12.0
G15		R1	0.5	SF	35	BENT	16	NaCl	7	135	12.3
G16		R1	0.7	SF	20	DE	20			125	12.3
G17		R1	0.6	SAND	40	BENT	2	PERL	9	102	13.7
G18		R1	0.8	SF	35	ALOH	4			55	15.9
J1	Unadeep "J"	R1	0.3							43.5	15.4
J2		R1	0.2	FA	79					75	15.0
J3		R1	0.2	BENT	2	PERL	9			106	13.3
J4		R1	0.3	BENT	4					65	14.2
J5		R1	0.3	BENT	8					86	13.1
J6		R1	0.2	NaCl	16					43.5	15.7
J7		R1	0.2	KCl	16					43.5	15.7
J8		R1	0.3	NaCl	4.4					43.5	15.5
J9		R1	0.1	SSS	2					90	12.3
J10		R1	0.3	ALOH	5					44	15.4
L1	1:1 Lime:SF	R1	0.4							90	12.0
L2		R1	0.4	PERL	9	BENT	2			110	10.8
L3	29:71 Lime:FA	R1	0.3	FA	79					130	11.8
L4		R1	0.2							71	12.8
S1	Slag	R1	0.8	SF	35					54	15.9
S2	(Univ. Atlas)	R1	0.6	SF	35	FA	80			93	15.1
A1	Fondu (LaFarge)	R2	1.8							50	14.9
A2		R2	1.5	FA	85					80	14.8
A3		R2	1.5	SF	50	FA	50			80	15.0
OR1	Furfuryl	CAT	0.52	COAL	160					None	10.5
OR2	Alcohol	CAT	0.52	COAL	220	PHEN	50			None	10.6
P1	Potassium aluminum fluophosphate cement with high catalyst concn.										13.5
P2	Potassium aluminum fluophosphate cement with low catalyst concn.										13.4

TABLE 4 (Cont'd)

ADDITIVE CODES:	<u>Code</u>	<u>Material</u>
	ALOH	Aluminum Hydroxide, $\text{Al}(\text{OH})_3$
	BENT	Bentonite
	CAT	Acid Salt Catalyst
	COAL	Powdered Coal
	DE	Diatomaceous Earth
	FA	Fly Ash
	GILS	Gilsonite
	ILLM	Ilmenite
	PERL	Expanded Perlite
	PHEN	Phenolic Resin, Liquid
	R1	Retarder-Proprietary blend of sugar and lignin derivatives.
	R2	Retarder-Proprietary blend of lignin and inorganic salts.
	SF	Silica Flour - less than 200 mesh, avg. < 10 micron size.
	SAND	Medium Fine Silica - from 70 to 200 mesh, avg. 100 micron size.
	SSS	Sodium Metasilicate, Solid

TABLE 5

Compressive strengths of systems evaluated in static brine exposure testing program. System descriptions are given in Table 4. All values are in lbs/sq. in. and were obtained after curing at the specified conditions.

System	Fresh Water		Lt. Brine(325°C)*		Hv. Brine(325°C)*		Dry Heat(325°C)
	1 Day(66°C)	3 Day(300°C)	7 Day	28 Day	7 Day	28 Day	28 Day
G1	6700	3650	1925	1150	3400	950	5350
G2	5375	3800	1475	1100	2325	900	3850
G3	5450	5250	4525	6975	5675	5875	4475
G4	5250	4600	7450	6840	7100	4800	7450
G5	2725	5725	4800	2975	5875	1750	2100
G6	2325	1350	3925	2225	3325	1150	3025
G7	7200	4825	5775	5175	4650	4275	5250
G8	7800	4900	6725	6850	6500	5325	8150
G9	5125	-Not Run-	5475	6916	4450	4425	6400
G10	7550	-Not Run-	8325	8325	6675	6450	9375
G11	3650	4500	2800	2750	2575	1350	3150
G12	4950	4600	3275	3275	3050	2550	2275
G13	4925	-Not Run-	3050	2650	3025	1875	2100
G14	2450	880	1125	1425	1725	1725	1575
G15	750	1150	950	800	1650	600	1675
G16	1950	1375	1825	2400	1325	1100	1725
G17	2350	1225	4300	3775	350	400	2100
G18	5100	-Not Run-	7825	7825	6875	4850	5275
J1	2700	5600	3500	5175	3600	4875	-Not Run-
J2	2100	-Not Run-	3975	3300	3000	2575	425
J3	1625	975	1000	525	475	375	725
J4	1900	2975	2050	1625	1150	1800	1025
J5	1850	1325	2625	175	287	200	2550
J6	1925	4850	4675	4125	4225	5325	1950
J7	1425	-Not Run-	4500	3800	3525	4920	1825
J8	1375	-Not Run-	4325	4650	3250	5200	1725
J9	525	825	1925	875	2000	800	600
J10	1400	-Not Run-	8125	4950	6600	5575	1700
L1	2125	1150	1250	850	1550	1170	2925
L2	800	550	525	200	350	75	2000
L3	1925	1825	1625	175	1400	125	700
L4	1100	1800	1300	100	1275	100	450
S1	5025	6075	1100	5775	6250	7525	3450
S2	2675	4150	3775	1975	3200	1500	3000
A1	1325	1100	550	975	1000	250	5975
A2	625	1025	1575	1250	1675	1025	500
A3	1000	2475	1500	1175	2425	3150	2650
OR1	2400	2125	5225	4200	4775	2425	-Burned-
OR2	2900	3000	4150	-Not Run-	2300	1700	-Burned-
P1	1350	-Not Run-	425	200	200	250	-Not Run-
P2	850	-Not Run-	525	100	475	150	275

*NOTE: Brine compositions given in Table 2

TABLE 6

Permeabilities of systems evaluated in static brine exposure testing program. System descriptions are given in Table 4. All values represent permeability to water after curing at specified conditions.

System	Fresh Water(66°C)	Light Brine(325°C)*		Heavy Brine(325°C)*		Dry Heat(325°C)
	1 Day	7 Day	28 Day	7 Day	28 Day	28 Day
G1	< .0002	0.096	1.17	0.095	1.69	0.003
G2	< .0002	0.038	1.90	0.055	1.38	0.004
G3	< .0002	0.009	0.10	0.007	0.061	0.002
G4	< .0002	0.069	0.026	0.009	0.071	0.003
G5	.0003	0.015	0.85	0.008	0.69	0.004
G6	.0005	0.022	0.11	0.021	0.063	0.003
G7	< .0002	0.016	0.41	0.004	0.089	0.002
G8	< .0002	0.007	0.28	0.030	0.070	0.005
G9	< .0002	0.020	0.051	0.080	0.024	-Cracked-
G10	< .0002	0.012	0.039	0.025	0.052	0.006
G11	< .0002	0.011	0.018	0.049	0.051	-Broken-
G12	< .0002	0.008	0.027	0.023	0.011	0.003
G13	< .0002	0.007	0.014	0.009	0.013	0.011
G14	.0007	0.025	0.27	0.097	0.13	0.011
G15	.0006	0.048	0.49	0.089	0.46	-Broken-
G16	.001	0.025	0.37	0.14	0.36	0.010
G17	.005	0.052	0.42	0.29	1.50	0.016
G18	< .0002	0.003	0.020	0.005	0.018	0.001
J1	< .002	0.021	0.051	0.021	0.027	-Not Run-
J2	.0003	0.002	0.014	0.003	0.010	0.037
J3	.0006	0.133	0.14	0.34	1.52	0.44
J4	< .0002	0.131	0.14	0.136	0.22	0.009
J5	< .0002	0.093	2.54	0.64	1.25	0.034
J6	< .0002	0.023	0.053	0.033	0.14	0.011
J7	< .0002	0.041	0.047	0.041	0.048	0.012
J8	< .0002	0.018	0.028	0.036	0.041	0.009
J9	.0009	0.22	0.19	0.172	0.30	-Broken-
J10	< .0002	0.11	0.037	0.005	0.035	0.008
L1	.0004	0.37	0.27	0.13	0.34	0.023
L2	.0053	0.42	0.36	0.37	3.04	0.042
L3	.0008	0.047	-Not Run-	0.010	-Not Run-	-Broken-
L4	.0008	0.11	3.8	0.015	-Not Run-	-Broken-
S1	< .0002	0.013	0.018	0.011	0.034	0.005
S2	.0004	0.004	0.006	0.005	0.010	0.004
A1	0.05	1.47	1.38	0.4	> 10	0.19
A2	0.33	0.12	0.75	0.030	0.95	1.35
A3	0.19	0.15	0.148	0.031	0.037	0.24
OR1	0.002	0.004	0.001	0.003	0.001	-Burned-
OR2	0.007	0.003	-Not Run-	0.001	0.002	-Burned-
P1	0.006	0.61	0.24	0.28	0.042	-Not Run-
P2	0.011	0.72	0.022	0.13	0.047	0.64

*NOTE: Brine compositions given in Table 2

TABLE 7

X-ray diffraction analyses of selected cement systems after exposure at specified conditions. System descriptions are given in Table 4. Brine compositions given in Table 2 (Heavy = "Salton Sea", Light = "East Mesa").

<u>System</u>	<u>Exposure Time(Days)</u>	<u>Brine</u>	<u>Qualitative Composition</u>	<u>Compressive Strength Range</u>
G1	28	Heavy	Xonotlite; 3.50 Å Unident.	Medium Low
G3	28	Dry	Non-crystalline	High
G5	28	Heavy	Tobermorite; Xonotlite	Medium
G6	7	Heavy	Xonotlite	High
G6	28	Heavy	Xonotlite	Medium
G15	7	Heavy	Xonotlite	Medium
G15	28	Heavy	Xonotlite	Low
G17	7	Light	Xonotlite	High
G17	7	Heavy	Kilchoanite; C_8S_5	Low
G17	28	Heavy	Xonotlite; kilchoanite	Low
G18	7	Light	Xonotlite	High
J2	28	Dry	Non-crystalline	Low
J3	7	Heavy	Scawtite; Rosenhahnite	High
J5	7	Light	Scawtite; Tobermorite	Low
J5	7	Heavy	Scawtite; Tobermorite	Low
J5	28	Heavy	Scawtite; Truscotite	Low
J9	28	Heavy	Scawtite; Truscotite	Medium Low
L2	7	Heavy	Scawtite; Tobermorite	Low
S1	7	Light	Tobermorite; Unidentified	High
S1	28	Light	Xonotlite	High

TABLE 8

Effect of various formation materials upon the integrity of a selected cement system. Additive codes are given at the end of Table 4.

No.	Cement	Additives(Percent BWOC)		% Water		Formation Material	Amt.
		Code	Amt.	Code	Amt.		
F1	Permanente "G"	R1	0.6	SF	35	84 Silica Sand	100
F2						84 Limestone	100
F3						100 Hard Clay	100
F4						84 Bright Angel Shale	100
F5						84 Argillaceous Shale	100
F6						84 Chiastolic Slate	100
F7						84 Graywacke	100
F8						84 Tuff	100
F9						84 Andesine	100
F10						84 Oligoclase	100
F11						84 Anorthite	100
F12						84 Serpentine	100
F13						84 Granite	100

PERMEABILITY DATA (millidarcies to water):

No.	Fresh Water(66°C)	Light Brine(325°C)		Heavy Brine(325°C)		Dry Heat(325°C)
	1 Day	7 Day	28 Day	7 Day	28 Day	28 Day
F1	.0002	0.021	0.012	0.010	0.004	0.001
F2	.0002	0.015	0.032	0.016	0.063	0.002
F3	.0004	0.036	0.16	0.045	0.076	0.001
F4	.0002	0.011	0.010	0.010	0.009	0.003
F5	.0002	0.010	0.011	0.005	0.013	0.002
F6	.0002	0.008	0.012	0.010	0.011	0.002
F7	.0002	0.011	0.010	0.011	0.014	0.002
F8	.0002	0.014	0.013	0.015	0.012	0.003
F9	.0002	0.012	0.017	0.013	0.013	0.002
F10	.0002	0.013	0.011	0.011	0.012	0.004
F11	.0002	0.011	0.014	0.011	0.018	0.003
F12	.0002	0.026	0.046	0.026	0.084	0.008
F13	.0002	0.019	0.015	0.010	0.012	0.002

COMPRESSIVE STRENGTH DATA (pounds per square inch):

No.	Fresh Water(66°C)	Light Brine(325°C)		Heavy Brine(325°C)		Dry Heat(325°C)
	1 Day	7 Day	28 Day	7 Day	28 Day	28 Day
F1	6700	6300	5400	5325	4350	9125
F2	6275	7500	5425	6575	4725	7670
F3	3075	1700	1575	1975	1825	3675
F4	5725	6225	4750	4850	5100	6850
F5	5250	5425	4425	4225	4975	6100
F6	5525	5725	5600	3725	4950	7000
F7	5650	5100	5025	5025	6250	6075
F8	5700	5750	6025	5100	6300	6200
F9	4425	5125	5175	4325	5850	5350
F10	5250	6900	5750	4050	5425	8450
F11	5450	6350	5600	5875	6575	6075
F12	5200	6575	8075	5275	5975	6150
F13	5975	5050	6025	5350	4900	6725

TABLE 9

Results of corrosion tests run for Dowell by Huntington Alloys. Materials are candidates for use in construction of geothermal simulator (D-BETA). Test fluid consisted of an aqueous brine containing 25% NaCl and 3% CaCl₂. All tests run at 316°C with oxygen present.

<u>Alloy</u>	<u>Corrosion Rate (mils per year)</u>		<u>Pitting</u>
	<u>Initial Exposure (48 hr)</u>	<u>Subsequent Exposure (92 hr)</u>	
Monel 400	14.58	6.28	None
Monel 400	19.90	5.84	None
Inconel 600	1.37	1.14	None
Inconel 600	0.76	1.46	None
Inconel 625	0.00	0.56	None
Inconel 625	0.00	0.40	None
Steel 1020	339.06	Not Run	Severe
Steel 1020	276.46	Not Run	Severe

TABLE 10

Cement systems studied in the preparation and evaluation of scawtite. Additive codes given at end of table. All amounts are given as percentage by weight of cement (BWOC).

No.	Cement	Carbonate Added		Other Additives				Percent Water
		Formula	Amt.	Code	Amt.	Code	Amt.	
1	Oklahoma "H"	CaCO ₃	2	SF	30			56
2	Oklahoma "H"	CaCO ₃	5	SF	30			56
3	Oklahoma "H"	CaCO ₃	10	SF	30			56
4	Oklahoma "H"	CaCO ₃	2	SF	30	SSS	2	100
5	Oklahoma "H"	CaCO ₃	5	SF	30	SSS	2	100
6	Oklahoma "H"	CaCO ₃	10	SF	30	SSS	2	100
7	Oklahoma "H"	NaHCO ₃	1	SF	35	SSS		80
8	Oklahoma "H"	NaHCO ₃	2.5	SF	35			80
9	Oklahoma "H"	NaHCO ₃	5	SF	35			80
10	Oklahoma "H"	Na ₂ CO ₃	1	SF	35			80
11	Oklahoma "H"	Na ₂ CO ₃	2.5	SF	35			80
12	Oklahoma "H"	Na ₂ CO ₃	5	SF	35			80
13	Oklahoma "H"	Na ₂ CO ₃	1	SF	35	R1	0.2	80
14	Oklahoma "H"	Na ₂ CO ₃	2.5	SF	35	R1	0.2	80
15	Oklahoma "H"	Na ₂ CO ₃	5	SF	35	R1	0.2	80
16	Oklahoma "H"	NaHCO ₃	10	SF	35	R1	0.5	50
17	Oklahoma "H"	NaHCO ₃	25	SF	35	R1	0.5	50
18	Oklahoma "H"	NaHCO ₃	50	SF	35	R1	0.5	50

Additive Codes: SF = Silica flour

SSS = Sodium Metasilicate, Solid

R1 = Retarder (proprietary blend of sugar and lignin derivatives)

TABLE 11

Preparation and evaluation of scawtite. Results of curing systems outlined in Table 10 at various conditions of time and temperature. All systems cured at 3000 psi curing pressure. Semi-quantitative scawtite analysis by x-ray diffraction.

System No.	Curing Conditions		Compressive Strength (PSI)	Water Permeability (md)	Percent Scawtite
	Time (HRS)	Temperature (°C)			
1	72	232	2090	Not Run	< 15
2	72	232	2500	0.003	< 15
3	72	232	4250	0.005	< 15
4	72	232	600	Not Run	10-30
5	72	232	1415	0.035	10-30
6	72	232	1465	0.024	0
7	72	232	Not Run	Not Run	< 15
8	72	232	Not Run	Not Run	10-30
9	72	232	Not Run	Not Run	10-30
10	72	232	Not Run	Not Run	Trace
11	72	232	Not Run	Not Run	< 15
12	72	232	Not Run	Not Run	10-30
16	72	232	2910	Not Run	25-100
17	72	232	5990	Not Run	25-100
18	72	232	1760	Not Run	0
1	72	316	2750	0.017	0
2	72	316	2375	0.017	0
3	72	316	2125	0.015	0
4	72	316	725	0.127	0
7	72	149	Not Run	Not Run	0
8	72	149	Not Run	Not Run	0
9	72	149	Not Run	Not Run	Trace
10	72	149	Not Run	Not Run	0
11	72	149	Not Run	Not Run	0
12	72	149	Not Run	Not Run	0
13	24	149	Not Run	Not Run	0
14	24	149	Not Run	Not Run	0
15	24	149	Not Run	Not Run	0

TABLE 12

THICKENING TIME DATA FOR FURFURYL ALCOHOL POLYMERS

<u>System Description</u>	<u>Bottom Hole*</u> <u>Pressure (psi)</u>	<u>Surface**</u> <u>Pressure (psi)</u>	<u>Time To***</u> <u>Reach Bottom (Min)</u>	<u>Bottom Hole****</u> <u>Temperature (°F)</u>	<u>Thickening*****</u> <u>Time</u> <u>Hours:Min</u>
250 mls Furfuryl Alcohol plus 250 mls Experimental Resin 4607 plus 300 grams <20 mesh coal	5300	2000	34	300	+6:00
250 mls Furfuryl Alcohol plus 250 mls Experimental Resin 4607 plus 300 grams <20 mesh coal plus 1 mls ZnCl ₂ solution	5300	2000	34	300	+6:00
250 mls Furfuryl Alcohol plus 250 mls Experimental Resin 4607 plus 300 grams <20 mesh coal plus 5 mls ZnCl ₂ solution	5300	2000	34	300	1:00

* Pressure at which the test remains throughout the entire test, after the first 34 minutes.

** Pressure at which the test starts.

*** Time required to go from 80°F starting temperature to final temperature of 300°F.

**** Temperature at which the test remains throughout the entire test, after the first 34 minutes.

***** Time required for the system to achieve a viscosity of 100 poise.

Appendix 4

Quarterly Technical Progress Report
March-May, 1978

on

HIGH TEMPERATURE CEMENTING MATERIALS
FOR COMPLETION OF GEOTHERMAL WELLS

to

BROOKHAVEN NATIONAL LABORATORY

June 15, 1978

by

Rustu S. Kalyoncu
and
M. Jack Snyder

Under Contract No. 420825-S

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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
BA	- Boric Acid
t_T	- Thickening Time
t_s	- Setting Time
W/C	- Water to Solids Ratio
Uc	- Unit of Consistency

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HIGH TEMPERATURE CEMENTING MATERIALS
FOR COMPLETION OF GEOTHERMAL WELLS

Quarterly Technical Progress Report
March-May, 1978

INTRODUCTION AND SUMMARY

Upon the completion of Phase I and Phase II studies and enhancement of efforts in Phase III, investigations have resulted in significant advances in the evaluation and characterization of promising cementing compositions. A number of compositions made up of Class J oil well cement, Silica flour, Blast Furnace slags and pozzolan were evaluated in terms of their thickening times, strength development, permeability and cement-to-metal casing bond strength.

Cementing compositions with 40 percent or more cement (Class J, Class H or Class G) had average thickening time at 400 F and 10,000 psi less than two hours. This was somewhat lower than expected as preliminary thickening times were estimated by autoclaving the samples at 400 to 450 F and saturated steam pressure at these temperatures. After 3 to 4 hours of autoclaving all of these compositions exhibited consistencies of 100 Uc or below. It was only logical to assume that these compositions would at least have thickening times of similar magnitude as under static conditions if not somewhat longer. In any case, a number of new compositions with 30 percent cement have been prepared for evaluation. The thickening times of these compositions are presently being determined.

Outside of the relatively low thickening time values all the cementing compositions with 30 to 50 percent cement contents exhibit strengths and other physical properties which meet or surpass the requirements of the RFP.

The discussion of the laboratory data follows.

PROGRAM SCHEDULE

This laboratory research program is comprised of four main work phases, namely:

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.

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 III: Evaluate Cements Selected on
the Basis of Their Performance in Phase II

In the Phase III work, cementing materials selected on the basis of their

performance in Phase II are subjected to a more detailed performance evaluation relating to their use in the lining of geothermal wells. Specifically, considerations are given to:

- Task No. 1 - Setting behavior of the cementing materials
- Task No. 2 - Strength of the cementing materials
- Task No. 3 - Permeability of the cementing materials
- Task No. 4 - Bond strength of the cementing materials to the steel casing
- Task No. 5 - Corrosion of the steel well casing by the cementing media
- Task No. 6 - Compatibility of cementing materials with drilling muds.

In all cases, the effect of prolonged exposure to the down-hole, geothermal well environment on the properties and behavior of interest are examined.

For this period the work was involved in various tasks of Phase III. Summary of progress follows.

CURRENT PROGRESS

Phase III studies have been underway the last two months and progress has been made in a number of tasks identified under these phase studies. Data have been gathered in the following tasks:

- Task No. 1 - Setting behavior of the cementing materials
- Task No. 2 - Strength behavior of the cementing materials
- Task No. 3 - Permeability of the cementing materials
- Task No. 4 - Bond strength of the cementing materials to the steel casing
- Task No. 5 - Corrosion of the steel well casing by the cementing medium
- Task No. 6 - Study of compatibility of cementing materials with drilling muds.

Tasks No. 1. Setting Behavior-Thickening Time Tests

A high-pressure and temperature Thickening-Time Tester is used to determine the length of time a given cement slurry remains in a fluid state

(pumpable state) under a given set of thermal and pressure conditions and thus to compare with various cements.

Briefly, the procedure is to prepare the slurry to be tested, place it in the Thickening-Time Tester (high temperature-pressure consistometer), apply pressure and increase temperature until desired conditions are reached, and record the consistency as a function of time.

Complete details of the procedure with various schedules are given in API code RP 10B titled "Recommended Practice for Testing Oil Well Cements".

The High Pressure-Thickening Time Tester consists of a rotating, cylindrical slurry container equipped with a stationary-paddle assembly, all enclosed in a pressure chamber designed for a working pressure of 25,000 psi at a maximum temperature of 400 F. Pressure is generated by an air operated hydraulic pump and a complete hydraulic system with the normal reservoir, piping, valves, filters and other required items. Heat is supplied by a 3,000 watt, internal-tubular heater controlled by a variable transformer and a Pyrometer Controller. Thermocouples are provided for determining the temperature of the oil bath and of the cement slurry. The slurry container is rotated at a constant speed of 150 rpm by a motor and appropriate gear reduction. The consistency of the cement slurry is indicated and recorded as a DC voltage obtained from a potentiometer mechanism within the pressure cylinder, which contains a standardized torsion spring to resist the rotating tendency of the paddle. This rotational tendency is proportional to consistency of the cement slurry. Valves, switches, pilot lights and other accessories are provided to make a completely integrated instrument. It is enclosed in a stainless steel cabinet with overall dimensions 60" high X 33" wide X 29" deep.

The thickening-time tests for the cement slurries are being carried out at Dowell Laboratories, Tulsa, Oklahoma. High pressure and temperature consistometer used is manufactured by Chandler Engineering Co., Tulsa, Oklahoma.

Since there is no API schedule describing the thermal and pressure conditions of interest to this program as may be encountered in geothermal wells, a modified version of schedule 32 is employed in these experiments. Table 1 is schedule 32 as described by API code RP 10B.

The heating rate of the cementing composition in the high-temperature and pressure consistometer was about 7.5 F per minute. The final thermal and pressure

TABLE 1. 20,000 FEET (6100 m) CASING-CEMENTING
WELL-SIMULATION TEST-SCHEDULE 32 (PARTIAL)

Time, Min.	Pressure, psi kg/cm ²	Temperature Gradient, deg F/100 ft. depth			
		1.1		1.5	
		F	C	F	C
0	2000 (140)	80 (27)		80 (27)	
2	2900 (204)	88 (31)		92 (33)	
4	3800 (268)	96 (36)		104 (40)	
6	4700 (332)	104 (40)		117 (47)	
8	5600 (396)	113 (45)		129 (54)	
10	6500 (460)	121 (49)		141 (61)	
12	7500 (524)	129 (54)		153 (67)	
14	8400 (588)	137 (58)		165 (74)	
16	9300 (651)	145 (63)		177 (81)	
18	10200 (715)	153 (67)		190 (88)	
20	11100 (779)	161 (72)		202 (94)	
22	12000 (843)	169 (76)		214 (101)	
24	12900 (907)	178 (81)		226 (108)	
26	13800 (971)	186 (86)		238 (114)	
28	14700 (1035)	194 (90)		251 (122)	
30	15600 (1099)	202 (94)		263 (128)	
32	16500 (1163)	210 (99)		275 (135)	
34	17500 (1227)	218 (103)		287 (142)	
36	18400 (1291)	226 (108)		299 (148)	
38	19300 (1355)	235 (113)		311 (155)	
40	20200 (1418)	243 (117)		324 (162)	
42	21100 (1482)	251 (122)		336 (169)	
44	22000 (1546)	259 (126)		348 (176)	
Heating Rate, deg F/min.		4.07		6.09	
deg C/min.		2.25		3.39	
Static bottom-hole temp.		300(149C)		380(194C)	

NOTE 1: Final temperature and pressure should be held constant to completion of test, within +2 F(+1 C) and +100 psi(+7 kg/cm²), respectively.

NOTE 2: Schedule developed from water-base mud system data.

From 5-75, Cem.

Sec. II-C sup. 1 RP 10B

condition was usually attained in 45 to 50 minutes, then was held constant for the duration of the experiment. Cementing compositions with 40 to 50 Class J oil well cements as the main hydraulic component exhibited average thickening times of 120 minutes, which is considerably lower than indicated by the preliminary laboratory experiments performed in sealed glass ampoules. Most of these compositions exhibited 3 to 4 hours thickening times in sealed ampoules. It was anticipated that the dynamic values, measured with the high-temperature and pressure consistometer, would at least be just as high if not somewhat higher. This anomaly will be examined more closely.

Presently, cementing compositions with 30 percent cement contents are being evaluated. These are expected to have considerably longer thickening times. The physical properties of these compositions are well within the requirements set by the RFP as discussed in the proceeding sections.

Task No. 2. Measurement of Strength Behavior

The strength development of cements as a function of curing time has been determined for a number of cementing compositions for 1-day and 7-days curing times. Specimens prepared for this task are 1 inch diameter by 1 inch long cylinders. The specimen preparation and compressive strength measurements are carried out in the following manner:

- (1) Cast specimens in cylindrical molds (1 inch diameter by 6 inches long) at room temperature and ambient pressure.
- (2) Immediately place molds in autoclaves and cure hydrothermally (24 hours) at a temperature to be determined.
- (3) Remove specimens from autoclave and demold.
- (4) Cut 1 inch long specimens from 6 inch long cylinders with cut-ends flat and parallel.
- (5) Determine compressive strength of three specimens of each cement at 300 F temperature as an indication of the strength of the cementing material 24 hours after placement.
- (6) Store the remaining specimens (uncut) in hydrothermal reaction vessels for exposure times of 1 week, 1 month, and 3 months. Pressure will correspond to the steam at that temperature.

- (7) After the desired exposure period remove specimens from the reaction vessel and cut specimens (per Step 4).
- (8) Place the 1 inch diameter X 1 inch long cylindrical specimen in the pressure can assembly. The pressure can and will be filled with water.
- (9) Heat the pressure can and specimen to the temperature to which the specimen was exposed in Step 6, and await temperature equilibration
- (10) Load specimen (uniaxial compression) to failure and calculate compressive strength.

Measurement of compressive strengths of specimens is accomplished in a specially constructed temperature and atmosphere-controlled cell which can be mounted on the strength testing machine.

In a program for the U.S. Atomic Energy Commission, completed at Battelle in 1969, a technique was developed for measuring the strength and elastic properties of heated portland cement concrete at temperatures up to 500 F under saturated steam pressures. These measurements were carried out in a specially designed pressure-can assembly shown in Figure 1. The pressure can is constructed from 3/8 inch thick stainless steel and has a removable lid for access to the specimen chamber. In Figure 1, a 4 X 8 inch concrete cylinder is represented as the test specimen, although other specimen geometries can be used. A stainless-steel bellows assembly in the lid permits the transfer of a uniaxial compressive load to the specimen, while the specimen is at temperature under saturated steam pressure.

A large Nichrome split-shell furnace (not shown in Figure 1) is used around the body of the pressure can to gain the desired temperature in the specimen. Heat losses from the ends of the can are minimized by the use of cartridge heaters in the bottom and insulation at the top of the can. The can is fitted with pressure-tight thermocouple glands, a pressure gauge, a pressure-relief valve, and a safety-blowout disc.

In practice, the pressure-can and furnace assembly is positioned on an Instron testing machine for strength testing. The pressure can is filled prior to heating with water or another solution. A sufficient time is then allowed for temperature and pressure equilibration prior to application of the load.

Figure 1. Schematic of the pressure-can test assembly used in measuring the compressive strength of concrete at elevated temperatures under saturated steam pressure (shown with 4x8 in. concrete cylinder specimen).

The compressive strength data on various cementing compositions, after 1- day 7-day autoclave hydration at 450 F, are depicted in Tables 2 through 5. All the strengths are well above the required minimum strength of 1000 psi. No deterioration of strength is observed after 7 days of autoclaving. Experiments are currently underway for longer autoclaving effects on the compressive strengths. Some of the measurements have been made both at room temperature and at 300 F (and saturated steam pressure) using the high temperature and pressure cell. The strength reduction observed due to change in the testing conditions is not as large as is the case with conventional portland cements and portland cement concretes. This could be attributed to the presence of significant amounts of essentially non-hydraulic additives whose reactivities increase as a function of temperature.

TABLE 2. COMPRESSIVE STRENGTHS OF COMPOSITIONS WITH
50 PERCENT CLASS J OIL WELL CEMENT
AT 450 F AFTER 1 DAY HYDRATION

Cement Composition	Amounts, %	Admixture *	W/S	Compressive Strength, Room Temp. (psi)
SF	25	CMC	0.6	2750
BFS	25			
L	25	CMC	0.7	890
SF	25			
SF	25	CMC	0.5	3821
P	25			
P	25	CMC	0.6	3965
BFS	25			
SF	15	CMC	0.6	3248
P	10			
BFS	25			
SF	25	BA	0.5	2000
BFS	25			
L	25	BA	0.6	1804
SF	25			
SF	25	BA	0.55	31
P	25			
P	25	BA	0.6	138
BFS	25			
SF	15	BA	0.6	1174
L	10			
P	25			
SF	15	BA	0.5	2269
L	10			
BFS	25			
SF	15	BA	0.5	172
P	10			
BFS	25			

* Admixture Dosages

CMC - 0.5% weight of solids.

BA - 1.0% weight of solids.

TABLE 3. COMPRESSIVE STRENGTHS OF COMPOSITIONS WITH
40 PERCENT CLASS J OIL WELL CEMENT
AT 450 F AFTER 1 DAY HYDRATION

Cement Composition	Amounts, %	Admixture *	W/S	Compressive Strength, Room Temp. (psi)	Compressive Strength, 300 F-steam
SF	30	CMC	0.6	1912	
BFS	30				
L	30	CMC	0.7	1174	
SF	30				
SF	30	CMC	0.55	1918	
P	30				
P	30	CMC	0.65	3341	
BFS	30				
SF	20	CMC	0.6	2777	
P	20				
BFS	20				
SF	30	BA	1.0	1860	
BFS	30				
L	30	BA	1.0	1626	
SF	30				
SF	40	CMC	0.5	2276	2480
P	20				
SF	30	BA	0.55	75.40	
P	30				
P	30	BA	0.6		
BFS	30				
SF	20	BA	0.65	1429	
L	20				
P	20				
SF	20	BA	0.55	2447	

TABLE 4. COMPRESSIVE STRENGTHS OF COMPOSITIONS WITH
30 PERCENT CLASS J OIL WELL CEMENT
AT 450 F AFTER 1 DAY HYDRATION

Cement Composition	Amounts, %	Admixture *	W/S	Compressive Strength, Room Temp. (psi)	Compressive Strength, 300 F-steam
SF	40	CMC	0.5	1566	1236
P	30				
SF	30	CMC	.05	1895	1275
BFS	40				
P	30	CMC	0.5	4849	3215
BFS	40				
P	40	CMHEC	0.5	2745	1860
BFS	30				
SF	35	CMC	0.5	2486	1800
BFS	30				
B	5				
BFS	70	CMC	0.5	1038	1019
P	70	CMC	0.5	1908	1541
BFS	60	CMC	0.5	1836	1812
SF	10				
P	60	CMC	0.5	1864	1457
SF	10				

* Admixture Dosages

CMC - 0.5% by weight of solids.

CMHEC - 0.5% by weight of solids.

TABLE 5. COMPRESSIVE STRENGTHS OF COMPOSITIONS WITH
40 PERCENT CLASS J OIL WELL CEMENT
AT 450 F AFTER 7 DAY HYDRATION

Cement Composition	Amounts, %	Admixture *	W/S	Compressive Strength, Room Temp. (psi)
SF	30	CMC	0.5	2558
BFS	40			
L	30	CMC	0.5	1588
SF	30			
SF	30	CMC	0.5	1687
P	30			
P	30	CMC	0.5	3307
BFS	30			
SF	20	CMC	0.5	3188
P	20			
BFS	20			
SF	30	BA	0.5	1165
BFS	30			
L	30	BA	0.5	2263
SF	30			
SF	30	BA	0.5	1541
P	30			
P	30	BA	0.5	3104
BFS	30			
SF	20	BA	0.5	1138
L	20			
P	20			
SF	20	BA	0.5	2002
L	20			
BFS	20			
SF	20	BA	0.5	3142
P	20			
BFS	20			

TABLE 5. (Continued)

Cement Composition	Amounts, %	Admixture	W/S	Compressive Strength, Room Temp. (psi)
SF	60	CMC	0.5	
SF	20	CMC	0.5	1923
BFS	40			
SF	30	CMC	0.5	1472
BFS	30			
SF	40	CMC	0.5	1800
BFS	20			
SF	30	CMC	0.55	
P	30			
SF	60	BA	0.5	983
SF	20	BA	0.6	1580
BFS	40			
SF	30	BA	0.6	1443
BFS	30			
SF	40	BA	0.65	1232
BFS	20			
SF	30	BA	0.6	1400
P	30			

* Admixture Dosages

CMC - 0.5% by weight of solids.

BA - 1.0% by weight of solids.

Task No. 3. Measurements of Permeability

After curing at various temperatures and pressures for prescribed lengths of time, cementing specimens are subjected to permeability tests. One of the objectives of this program is to develop cementing materials of low permeability to liquids (maximum permeability of 0.1 md to water). Therefore, it is necessary to measure the permeabilities of candidate cementing materials.

The permeability measurements are made at room temperature using water and helium as the permeating media employing the apparatus shown in Figure 2 (a slightly modified version of this apparatus is used for liquid permeability measurements, as this apparatus is designed for a pressure gradient of not more than three atmospheres). Specimens of 1 inch diameter and 1/4 inch thick are used as permeability samples. The cylindrical-disc cement specimen is inserted in the specimen holders (A) and (B). A rubber gasket and a latex sealing material provide the seal between two ends of the specimen and the amount of fluid permeating through the material in a given time is measured. Permeability values are calculated from the experimental data employing Darcy's Law.

According to Darcy's Law:

$$K = 14,700 \frac{Q\mu L}{AP}$$

where:

- K= permeability in millidarcys (md)
- Q= fluid flow rate in ml/sec
- μ = fluid viscosity in centipoise (cp)
- L= Sample length in cm.
- A= sample cross-sectional area in cm²
- P= Differential pressure in psi.

Permeabilities (both liquid and gas) of a half dozen compositions after 24 hours hydration under autoclave conditions have been measured.

Liquid permeabilities are measured 100 psi pressure gradient.

Table 6 depicts some of the preliminary gas and water permeability values of a number of cements. As can be seen, compositions with increasing Blast Furnace slag contents increase in permeability.

Figure 2. Schematic drawing of the permeability apparatus.

TABLE 6. WATER AND HELIUM PERMEABILITIES OF SELECTED CEMENTING COMPOSITION AFTER 24 H. CURING AT 450 F AND SATURATED STEAM PRESSURE*

Composition	W/C	Admixture	He Permeability (md)	Water Permeability (md)
Class J - 50 Lime - 25 Silica Flour - 25	0.6	Boric Acid	9×10^{-3}	7×10^{-2}
Class J - 50 Lime - 25 Silica Flour - 25	0.7	CMC	5×10^{-2}	2×10^{-1}
Class J - 40 Silica Flour - 40 Pozzolan - 30		CMC	-	4.4×10^{-2}
Class J - 30 Pozzolan - 40 BFS	0.5	CMHEC	6×10^{-3}	2×10^{-2}
Class J - 30 Pozzolan - 40 Silica Flour - 30	0.6	CMC	-	3×10^{-1}

* Actual permeabilities are believed to be lower than the reported values as there are still some refinements to be made in the measurement techniques.

Task No. 4. Investigation of the Bond Between the Cementing
Material and the Steel Casing

This work is conducted using specially prepared specimens as shown in Figure 3. The specimens are prepared by inserting a 2 inch-long and 1/4 inch diameter steel rod in a 2 inch-long and 1 inch-diameter cylindrical specimen mold prior to casting the cement. The rod is parallel to the long dimension and coaxial with the longitudinal axis of the specimen. The cement is cast to a depth of 1 1/2 inch. The specimens are placed in the autoclave assembly and cured for a prescribed length of time at a pre-determined pressure and temperature.

For the cement-to-steel bond strength measurements the specimens are placed in the pressure-can assembly set up on the Instron machine. The pressure can and specimen then are brought up to the desired test temperature (with saturated steam in the pressure can) and temperature equilibrium is established. At this point the force required to move the steel rod through the cement specimen is measured. The bond strength is calculated as shear force necessary to move the steel rod through the cement divided by the interfacial surface area between the cement and the steel rod. The specimens described above proved most suitable for these experiments and no modifications had to be made in the specimen shape and size.

Figure 3. Proposed specimen configuration for investigation of bond strength between the cementing material and the steel casing.

TABLE 7. COMPRESSIVE STRENGTHS OF COMPOSITIONS WITH
40 PERCENT CLASS J OIL WELL CEMENTS
AT 450 F AFTER 1 DAY HYDRATION

Cement Composición	Amounts, %	Admixture*	W/S	Bond Strength, Room Temp. (psi)
SF	30	CMC	0.5	170
BFS	30			
L	30	CMC	0.5	204
SF	30			
SF	30	CMC	0.5	731
P	30			
P	30	CMC	0.5	595
BFS	30			
SF	20	CMC	0.5	140
P	20			
BFS	20			
SF	30	BA	0.5	97
BFS	30			
L	30	BA	0.5	13
SF	30			
SF	40	CMC	0.5	442
P	20			
SF	30	BA	0.5	22
P	30			
P	30	BA	0.5	182
BFS	30			
SF	20	BA	0.5	348
L	20			
P	20			
SF	20	BA	0.5	170
L	20			
BFS	20			
SF	20	BA	5	5

TABLE 8. COMPRESSIVE STRENGTH OF COMPOSITIONS WITH
40 PERCENT CLASS J OIL WELL CEMENT
AT 450 F AFTER 1 DAY HYDRATION

Cement Composition	Amounts, %	Admixture	W/S	Bond Strength, Room Temp. (psi)
SF	40	CMC	0.5	442
P	20			
SF	40	CMC	0.5	366
P	30			
SF	30	CMC	0.5	132
BFS	40			
P	30	CMC	0.5	159
BFS	40			
P	40	CMHEC	0.5	323
BFS	30			
SF	35	CMC	0.5	111
BFS	30			
B	5			
BFS	70	CMC	0.5	106
P	70	CMC	0.5	136
BFS	60	CMC	0.5	132
SF	10			
P	60	CMC	0.5	166
SF	10			

* Admixture Dosages

CMC - 0.5% by weight of solids.

BA - 1.0% by weight of solids.

Task No. 5. Corrosion of the Steel Well Casing by the Cementing
Medium-Task No. 6. Study of Compatibility of
Cementing Materials with Drilling Muds

Tasks No. 5 and 6 have not yet been started. Arrangements are being made to commence these two tasks.

Appendix 5

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

A quarterly 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

for the period
March 1 - May 31, 1978

June 14, 1978

Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

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

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

June 1978

The Pennsylvania State University

I. Introduction

The objectives of this work are to develop new high temperature cementing materials for geothermal wells. During this past quarter we have filled in more detail on phase stabilities in the low temperature regions for both the lime-magnesia-silica-water and the lime-alumina-silica-water systems. Continued property measurements including microhardness, viscosity and permeability on the cementitious materials are also reported. Parallel studies have continued using a variety of starting materials including commercial cements and natural mineral additives, with suitable compositional adjustments; and pure chemicals. This approach attempts to define stable equilibria, but apply the results to potential practical systems as quickly as possible.

II. Experiments in the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ System

A. Stock Chemical and Gel Starting Materials

A naturally-occurring form of silica, diatomaceous earth "tripoli" was used as the source of SiO_2 in experiments with stock chemicals under the hydrothermal conditions being investigated. This amorphous silica is known to be a high purity form of silica. The use of "tripoli" has confirmed under the PT conditions studied the stability of the phases xonotlite, chrysotile, talc, and truscottite. The rate of formation of the stable calcium silicate phases and phase assemblages appears to be enhanced by the use of tripoli. This is attributed to the fine particle size and amorphous nature of the material. Unlike other similar experiments using Minusil quartz, or calcium silicate gels, gyrolite has not been encountered with the use of tripoli, even in runs of short duration (5 to 7 days), confirming the

previous observation that the formation of gyrolite from other starting materials under the present hydrothermal conditions represents a metastable formation of this phase. The use of tripoli has also reduced the size of the composition region in which anhydrous monticellite has been encountered.

Hydrothermal reactions of longer duration have now been carried out to determine longer term stability. While previously-determined phase equilibria have been confirmed, these also appear to indicate that the anhydrous phase monticellite does occur as a stable phase. In the system at 400°C and 10,000 psi (68.9 MPa) monticellite occurs in stable equilibrium with both the hydrate species xonotlite and chrysotile (see Fig. 1). This conclusion is in agreement with the data of Petrovic (1973), who reported monticellite as a stable phase in the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ system at 350°C, and Roy (1956), who described hydrothermal synthesis of monticellite at 475°C.

Similar long term experiments (30 days) appear to indicate that the hydrous calcium magnesium silicate, tremolite, does not occur stably under the present hydrothermal conditions. The only phases which have been identified as reaction products with the tremolite composition are talc and xonotlite.

Slaughter, Kerrick and Wall (1957) have placed the reaction of the synthesis of tremolite as follows: talc + calcite + quartz $\rightarrow$ tremolite + CO_2 + H_2O at 440°C and 2 kb (28,800 psi). $X_{\text{CO}_2} = 0.5$ (X = mole fraction). The lower temperature limit is not known but the synthetic amphibole studies of Boyd (1959), at very high pressures where the fluid phase was pure H_2O , suggest that the present hydrothermal conditions may fall within the stability field of tremolite. The role of tremolite in the system therefore remains uncertain and further experiments are being performed.

Another series of hydrothermal experiments are being undertaken. These are being carried out at 10,000 psi and 300°C with similar compositions to those already being investigated at 10,000 psi and 400°C. These are being performed to determine phase stabilities at the lower temperature, and changes, if any, taking place from the higher temperature assemblages, particularly with respect to the stability of the calcium silicate hydrate species. Such experiments are necessary to permit collection of more comprehensive information on phase equilibria under a wider range of the

Figure 1. Compatibility relationships in the CaO-MgO-SiO_2 system at 400°C and 10,000 psi (68.9 MPa).

relevant hydrothermal conditions. They will also give information relevant to expected reaction products should calcium silicate cements be subjected to high Mg content geothermal fluids.

B. Class J Cement and Stock Chemicals as Starting Materials

Four samples lying on the xonotlite-chrysotile join (see Fig. 1, #18, 19, 19T, 20) were prepared using class J cement, MgO, CaO, and two forms of SiO₂: "tripoli" and 5μ Minusil. Hydrothermal curing conditions were 10,000 psi and 400°C for 36 days. As with the stock chemical starting materials the rate of formation of the stable phases in the samples using "tripoli" was enhanced. However, the microhardness values given in Table 3 for the Minusil-containing samples were twice those for the tripoli-containing samples. Even so, these samples are among the strongest made thus far using class J cement. Samples with the same composition are being treated hydrothermally to determine their longer term stability and strength.

In addition, two sets of samples with the same composition as above and a saturated NaCl solution rather than de-ionized water are being treated hydrothermally at 10,000 psi and 300 and 400°C respectively.

III. Experiments in the CaO-Al₂O₃-SiO₂-H₂O System

A. Stock Chemical and Gel Starting Materials

Fifteen mixtures prepared within this system were treated hydrothermally at 10,000 psi (68.9 MPa) for 48 days at 400°C and another set of 15 mixtures were treated at 300°C. The data indicate that, contrary to what had been previously reported, truscottite is apparently not stable at 400°C. The amount of truscottite decreases with time and in some cases reacts completely with the other components in the sample and disappears. The hydrogarne⁺ phase hibschite became slightly more siliceous with increasing time. This was indicated by a 0.1 to 0.2 degree increase in 2θ values observed in the XRD patterns (anorthite peaks were used as the reference 2θ values). Figure 2 shows several new phases which crystallized during the 48 days that were not present after 10 days as is shown in Fig. 3. The reaction products shown in Table 1 for both 300°C and 400°C are valid for oxide-mixture starting materials since the gel-starting material resulted in crystallization of metastable phases in the system.

TABLE 1

Reaction Products from Stock Chemical Starting Materials in the System
 $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ for Hydrothermal Curing at 300°C and 400°C,
 10,000 psi for 48 days.

Composition Number	Temperature °C	Phases Obtained	Comments
1	300	not determined	
	400	wairakite + anorthite	
2	300	not determined	
	400	anorthite	
3	300	not determined	
	400	bicchulite + boehmite + $\text{C}_4\text{A}_3\text{H}_3$	
4	300	heulandite + epistilbite + truscottite	
	400	wairakite (?)	no quartz no truscottite
5	300	not determined	
	400	reaction very slow, did not react completely	
6	300	truscottite + epistilbite	
	400	anorthite + wairakite + quartz + truscottite	
7	300	not determined	
	400	reaction very slow, did not react completely	
8	300	anorthite + hexagonal anorthite + phase X (?) + hibsichte + minor amounts xonotlite	
	400	anorthite + hibsichte + xonotlite	
9	300	not determined	
	400	reaction very slow, did not react completely	
10	300	xonotlite + minor anorthite + minor hibsichte	
	400	anorthite + wairakite + truscottite	
11	300	xonotlite + truscottite	
	400	anorthite + xonotlite + unidentified phase	unidentified phase 20 values: 15.9, 18.3, 22.7, 23.2, 26.15, 26.8.
12	300	xonotlite + anorthite + hibsichte	
	400	xonotlite + hibsichte + anorthite	
13	300	hibsichte + anorthite + phase X (?) + xonotlite	
	400	hibsichte + anorthite + xonotlite	
14	300	truscottite + anorthite (?) + xonotlite	
	400	xonotlite + anorthite	
15	300	truscottite + anorthite (?)	
	400		

inate [ca 33.5 % CaO , 59.3% ($\text{Al}_2\text{O}_3 + \text{TiO}_2$), 4.2% SiO_2] and perlite. The samples were cured overnight at room temperature at >90% relative humidity then cured hydrothermally at 465 and 365°C; 1400 and 3000 psi pressure; and 14 and 21-days respectively as outlined in Table 2. After hydrothermal treatment samples Hyd-3, -4, and -5 disintegrated; samples Hyd-6, -7, and -8 were weak and very low density. The latter samples were prepared for permeability and microhardness measurements. The results of these measure-

Figure 4. Summary of previous work in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 300°C and 4000 psi (Barrer and Denny, 1961) and at 300°C and 14,700 psi (Koizumi and Roy, 1960).

Figure 5. Compatibility relationships within the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 300°C for 48 days.

TABLE 2
Reaction Products from Ca Aluminate Cement, Perlite,
and Minusil (Quartz) Starting Materials.

Comp. No.	w/s	Temp. °C	Pres. psi	Time days	Wt % SiO ₂ *	Phases Observed
HYD-3	0.80	465	1400	14	65	quartz + phase X + wairakite (?) + anorthite (?)
HYD-6	0.60	365	3000	21	65	quartz + phase X + wairakite + anorthite
HYD-4	0.80	465	1400	14	45	quartz + phase X + anorthite (with some peaks missing)
HYD-8	0.50	365	3000	21	45	phase X + wairakite + triclinic anorthite
HYD-5	0.80	465	1400	14	55	quartz + anorthite + hexagonal anorthite (?)
HYD-7	0.55	365	3000	21	55	quartz + phase X + wairakite + anorthite

*Compositions #3, #4, #5 made with 50% Ca aluminate cement + 50% Perlite (by weight). Compositions #6, #7, #8 made with 75% Ca aluminate cement + 25% Perlite (by weight). Five-micron Minusil was added to each of the samples above to bring the SiO₂ content to that listed above.

ments are given in Table 3. Because of the excess amount of mixing water required even for the 25% perlite samples, the next series of mixes have been prepared with 95 weight percent calcium aluminate cement, 5 percent perlite, and the SiO₂-content adjusted with 5μ quartz addition to give the same compositions as above. Note that samples Hyd-5 and Hyd-7 above correspond to the #1 composition made with stock chemicals as starting materials in Fig. 2.

IV. EQUIPMENT

Two new furnace elements and new furnace shells have been constructed for the Barnes 500-cc autoclaves (modified from the Barnes-Rocking Assembly). These new furnaces have a 6-inch i.d. and 12-inch length so that the entire vessel plus the cold-seal can be inserted into the furnace

TABLE 3
Summary of Data Measured on Geothermal Cement Products.

Sample	Composition	Hydro-thermal Treatment	Micro-hardness (kg/mm ²)	Intrinsic Permeability (darcys)
6T	67% Class J Cement 23% Tripoli 10% MgO w/c = 1.6	10,000 psi 400°C	5.09 (0.71)	
HYD-6	75g Ca Aluminate cement 25g Perlite 122.9g Minusil 133.8g H ₂ O w/c = 0.60	365°C 3000 psi	2.40 (0.91)	1.0 x 10 ⁻² @ 6 psi 1.7 x 10 ⁻² @ 15 psi
HYD-7	43% Ca Aluminate cement 14% Perlite 42% Minusil w/c = 0.55	365°C 3000 psi	1.05 (0.13)	1.0 x 10 ⁻² @ 6 psi 5.6 x 10 ⁻² @ 15 psi
HYD-8	53% Ca Aluminate 18% Perlite 29% Minusil w/c = 0.5	365°C 3000 psi	8.51 (0.77)	4.5 x 10 ⁻³ @ 6 psi 7.4 x 10 ⁻³ @ 15 psi
18G	85% Class J Cement 15% MgO w/c = 0.45	10,000 psi 400°C 36 days	18.49 (1.03)	
19G	70% Class J Cement 20% MgO 10% Minusil w/c = 0.45	10,000 psi 400°C 36 days	26.34 (2.07)	
19T	70% Class J Cement 20% MgO 10% Tripoli w/c = 0.8	10,000 psi 400°C 36 days	15.88 (1.45)	
20G	86% Class J Cement 10% MgO 4% CaO w/c = 0.45	10,000 psi 400°C 36 days	18.25 (1.91)	

for low temperature work or only the vessel body can be inserted for higher temperature runs. This new arrangement will greatly reduce the temperature

gradient between the inside and outside and between the top and bottom of the vessel. Temperature profiles of the vessel, both inside and outside will be made and reported later.

In order to measure water permeability directly, an apparatus has been constructed of a miscellaneous grade, 300-series austenitic stainless steel with a capacity of 500 ml and an upper pressure limit of 5000 psi (34.5 MPa) with a factor of safety = 4. Samples are presently being cured hydrothermally for testing within this water permeability apparatus.

V. Property Measurements

A. Permeability

In the water permeability cell which has been designed and put into operation pressures of 2000 and 4000 psi will be used to drive the water through the samples. Because of this there was some question as to the applicability of Darcy's law, which applies to the laminar flow regime. Within the laminar flow regime the velocity of flow is proportional to the first power of the hydraulic gradient. The Reynolds number, a dimensionless ratio of the inertial to viscous (resistive) forces, serves as a criterion to distinguish between laminar and turbulent flow regimes. This numerical concept has been applied to establish the limits for the flow regimes. A Reynolds number of 2000 or less is the upper limit for laminar flow in pipes. A Reynolds number of between 1 and 10 (Todd, 1963) is the upper limit for laminar flow in porous media. Up to this critical value the viscous forces predominate over the inertial forces. The Reynolds number is expressed as:

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

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

μ = viscosity of fluid (water) (1.005 cp @ 20°C
= 1.005 x 10⁻² g/(cm-sec) @ 20°C

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

D = characteristic length (hydraulic radius = area/wetted perimeter).

Several recommendations on the best characteristic length have been (a) the square root of the intrinsic permeability (Todd, 1963), and

(b) pore diameter of the sample. The intrinsic permeability of a poor aquifer is on the order of 10^{-11} cm² (Todd, 1963); the pore size of a hardened portland cement with the highest frequency is on the order of 20Å, 2×10^{-7} cm (Mikhail, Copeland and Brunauer, 1964). Both these characteristic lengths give a flow regime within the laminar region.

The medium pressure cell in which nitrogen gas is forced through the sample with a liquid permeability extrapolated was used to measure permeability for samples HYD-6 to HYD-8. These results are reported in Table 3. Note that the intrinsic permeabilities reported are those at 6 and 15 psi rather than the extrapolated liquid permeabilities. This was done because a proper seal with the O-ring was not achieved on these highly permeable samples. In order to utilize higher pressures, a smooth surface is necessary to have a proper seal.

B. Microhardness Measurement

Microhardness had been measured on the cementitious samples prepared using modified Ca aluminate and class J cement compositions. These data are given in Table 3. Note that the fine-grained tripoli-containing samples as well as the fine-grained perlite-containing samples generally had lower strengths than those made with 5-micron Minusil. Undoubtedly, only smaller contents of the low density materials are tolerated. Another comparison between the data presented here and that of the previous quarterly report shows that the strongest mixtures were HYD-1, #5, and #18, 19, and 20 and HYD-2.

C. Viscosity Measurements

The viscosity of a standard paratone oil from lot #22 has now been measured at room temperature, 60°C, and 105°C. Figure 6 for this newtonian fluid is shows the expected linear relationship between the rotational speed of the spindle and the rheological output.

As expected, the relationship between the speed and the output for the cementitious samples was generally non-linear. The modified Ca aluminate cement samples were additionally complicated by the fact that setting began before the testing was completed. The modified class J Cement samples

Figure 6. Rotational viscometer measurements.

as expected stayed quite runny throughout the testing. In these first tests using cement there is not a clear explanation for the details of the curvature shapes observed in Fig. 6. However, these results are being used to modify mix compositions, starting materials proportions, and other experimental factors.

Measurement times on the viscometer have been doubled as to what had been reported previously. It appeared that more time was necessary at each measurement to establish equilibrium.

VI. 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 6

SOUTHWEST RESEARCH INSTITUTE

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

TECHNICAL PROGRESS REPORT NO. 3

April - June 1978

SwRI Project No. 02-5083

to

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

July 15, 1978

APPROVED:

Prepared by:
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for

U. S. Lindholm, Director
Department of Materials Sciences

SAN ANTONIO, HOUSTON, CORPUS CHRISTI, TEXAS, AND WASHINGTON, D.C.

ABSTRACT

A research program to develop improved cements for use in geothermal well completions was begun in October 1977 at Southwest Research Institute. This third quarterly technical progress report includes work accomplished during the period April - June 1978. Selection has been made of several formulations for use over 218°C, and work is continuing to optimize the recipes for use over 315°C. Physical testing of the various formulations has included compressive and bond strengths, permeability to water and compatibility with drilling muds.

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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 well completions. This report describes the research carried out during the third quarter of our Brookhaven National Laboratory Contract No. 427964-S.

During the period of April 1 to June 30, 1978, a continuing review was made of hydrothermal cements, high-temperature cements, well cementing materials and methods of cementing. Various formulations of hydrothermal cements have been studied to optimize those which will be pumpable and set with sufficient strength at temperatures over 218°C and up to at least 315°C or higher. Physical tests have continued and long-term aging has begun.

II. REVIEW AND EVALUATION

We have continued to be alert for articles, etc., concerned with geothermal cementing, completion and, generally, with all aspects of geothermal activities. It has become a very minor part of the research effort at this time.

As part of the evaluation of the various hydrothermal cements and of cementing techniques in geothermal wells, several events have taken place. On June 6, a visit was made to the Los Alamos Scientific Laboratories (LASL) in Los Alamos, New Mexico, as guests of the Geothermal Energy Division. This group is experimenting with the injection of cold water into hot dry rock and recovering hot water at a temperature of about 200°C. Two wells are drilled, one is used to inject water, the other to recover it. The first well is also used to fracture the surrounding rock by hydraulic pressure. The cementing of the casing in the wells is performed as in other moderately hot geothermal wells. However, during the life of the injection well, the casing and cement are subjected to cycling as the formation is cooled, pumping is stopped to allow the formation to heat up again, and once more water injection is resumed. The effect of the cycling is to cause the casing to contract away from the cement behind it, causing water leakage up through this annulus which is formed. Problems such as these need to be remedied before full-scale application of the hot dry rock concept to power generation is made.

The API Task Group on Cements for Geothermal Wells was attended by SwRI representatives, W. A. Mallow and D. K. Curtice. This meeting was held in Tulsa, Oklahoma, June 20. Some 25 or 26 persons attended and reported on the

various aspects of geothermal well cements. It was a most informative meeting with some lively discussions generated. We have about 100 pages of transcriptions covering much of the meeting. As time permits, these will be put in good order and, if possible, copies can be made.

III. SOUTHWEST RESEARCH INSTITUTE HIGH-TEMPERATURE CEMENT RESEARCH

A. Formulation Optimization

1. General

Further optimization has taken place since December and, with modifications, we now have a stable hydrothermal cement for use at bottom-hole temperatures above 220°C. Consistometric (thickening time) tests have indicated that there should be no problems in the slurrying and pumping down hole or in the curing of this cement under geothermal conditions. Laboratory thickening and autoclave curing tests can only approximate bottom-hole conditions; however, we are confident that these formulations will prove adequate for temperatures above the minimum shown in Table I.

2. Recipes

The basic formulations of the hydrothermal cement systems for use at temperatures from about 70°C (similar to the SwRI original formulations) to over 260°C are listed in Table I. It can be seen that there are only small differences from formulation to formulation in relative amounts of the various ingredients. It should also be noted that the class of polyvalent metal salt is critical to the kinetics of the cement curing. The reactivity of aluminum oxide, hydroxides and hydrates varies greatly with their source and structure. Amphoteric aluminum hydroxide prepared by controlled hydrolysis of sodium aluminate is greatly different in activation temperature and reactivity with alkali silicates compared to hydrated alumina or anhydrous, calcined alumina.

For those interested, the commercially-available, stable hydroxide and hydrated-calcined aluminas are adequate for this cement technology.

TABLE I
SwRI Hydrothermal Cement Formulations

Ingredients*	Recipe - Parts or Grams				
	#1 at 66°C	#2 at 204°C	#3 at 260°C	#4 at 260°C	#5 at 260°C
Sand	50	50	50	50	50
Flour	25	25	25	25	25
Britesil	10	10	10	10	10
Anhydrous Sodium Silicate	10	10	10	10	10
Al(OH) ₃		7			
Al ₂ O ₃			5		
ZnO	5				
ZrO				7	
ZrCO ₃					10
H ₂ O	18	18	18	18	18

* See Table II for type and source.

Sources and types of our reagents are listed in Table II. The dry materials are usually blended and stored in a conventional manner, similar to portland cements, and mixed with water when needed.

The process of optimizing the formulations involves precise variations of each ingredient, in the amounts blended and choice or class of silicate and metal oxide employed. Use of different ratios of sodium silicate will increase or decrease the reactivity. Use of other zinc salts for instance, such as zinc carbonate or hydroxide, prepared with each different silicate will exhibit varied reactivities. The stoichiometries of the various formulations were thus empirically determined on the basis of final product properties.

Excesses of the silicates can reduce the dimensional stability of the hardened cement. Further, excesses of the polyvalent metal oxides may reduce or inhibit adhesion of the cement to interfaced surfaces. Under optimum hydrothermal conditions a recipe designed for it will perform admirably. However, under the conditions encountered in geothermal wells, a recipe needs to be designed for a minimum cure temperature and optimum pumpability characteristics for the worst conditions encountered.

With this in mind, we have presently extended our optimization procedures to find the "optimum formulation" for use over 316°C (600°F). In Table I, Recipe #3 and Recipe #5 appear to be the best for use over 316°C (600°F). These were pumpable for over 3 hours at this temperature. After 48 hours at 260°C (500°F), they were both in the gel state. Because of equipment problems, we have not yet been able to run 316°C consistometer thickening tests. We have determined, however, by use of a high-pressure pipe bomb, that the alumina (Al_2O_3), calcined RC-20 was still in a pumpable condition after 3 hours at 316°C.

TABLE II
Types and Sources of Ingredients

<u>Material</u>	<u>Type and Source</u>
Silica <u>Sand</u>	-20 + 60 mesh
Silica <u>Flour</u>	-200: 100% -325: 80%
Britesil C24	2.4/1 (SiO ₂ /Na ₂ O), 18% water, spray-dried microspheres (-100 mesh)
Anhydrous Sodium Silicate	3.22/1 (SiO ₂ /Na ₂ O), glass powder, -325 mesh
Al(OH) ₃	RH-31f hydrated alumina, Reynolds Aluminum Company
Al ₂ O ₃	RC-20 Calcined Alumina, Reynolds Aluminum Company
ZrO	Zirconia, -325 mesh, National Lead
ZrCO ₃	Cake, -325 mesh, National Lead
ZnO	XX60, New Jersey Zinc

B. Physical Properties Evaluation

1. Placement Ability

This has been discussed in the section above on the best formulations. Table III shows the results of the thickening time runs of acceptable recipes. The thickening time was gauged by the length of time it took the cement to reach 100 standard API units of consistency (Bearden, Bc units), extrapolated to 316°C, as recommended by API RP10B.

We are using a modified Autoclave Engineering, Inc., stainless steel autoclave, which can be used up to 400°C and 5300 psig before sensitizing the steel to cracking. We use a heating unit with automatic controllers reading both the heater temperature and inside autoclave temperature. A stirring paddle is brought through the head using water-cooled Teflon seals. The stirrer is turned by a DC motor, which is completely variable to spin the paddle from 1 to 500 rpm. Connected to the stirring rod outside of the autoclave are strain gauges which electronically convert torque into consistency of the slurry.

We are continuing to modify this unit to withstand the rigors of 300-400°C temperatures over periods of several hours. We have partially solved these problems by use of a stainless steel gasket between the cover and autoclave body and by water-cooling the head mechanisms.

2. Compressive Strength

Two-inch cubes have been made from the various formulations, cured for up to 28 days, and tested in a Model No. 977 Instron Load Cell Testing Machine. Table IV shows the test results of these specimens.

TABLE III

Results of Thickening Time Tests

<u>Recipe from Table I</u>	<u>Lowest Activation Temperature</u>	<u>Hours to 100 Units Consistency</u>
#1 - ZnO	60°C	6 Hrs
	90°C	2 Hrs
	120°C	3/4 Hrs
#2 - Al(OH) ₃	204°C	3 Hrs
#3 - Al ₂ O ₃	260°C	8 Hrs (48 hrs - gel only)
#4 - ZrO	260°C	6 Hrs (48 hrs - gel only)
#5 - ZrCO ₃	260°C	? (Hard in 48 hrs)

TABLE IV

Compressive Strengths of Various SwRI Formulations

<u>Recipe</u>	<u>Curing Temperature (°C)</u>	<u>Time of Cure</u>	<u>Compressive Strength (psi)</u>
ZnO	120	24 Hrs	>3000
	100	5 Days	2680
	218	7 Days	3800
	218	14 Days	5060
	218	28 Days	5440
Al(OH) ₃	120	5 Days	2675
	204	3 Days	3100
	260	3 Days	>3000
Al ₂ O ₃	260	2 Days Gel - No Tests	
	260	7 Days	>3000
ZrO	260	2 Days Gel - No Tests	
ZrCO ₃	260	2 Days	>3000

3. Bond Strength

Bonding tests have been made on specimens cured in steel cylinders. These are 3-in. ID, with a 1-in. steel pin centered by use of a machined base plate. The slurry is poured into this mold and cured at the appropriate temperature and condition. At the higher temperatures we have used 1-1/2-in. high-pressure steel pipe nipples, capped at one end, filled with slurry, capped securely, and placed in a furnace. These "bombs" have been successfully used to cure recipes up to 316°C. The large open molds can be used only to about 200°C. Shear bond test results are given in Table V.

4. Permeability to Water

Since the last quarterly technical report, we have not succeeded in decreasing the permeability of any of the formulations below 10 microdarcys. However, it is expected that the specimens aged for 28 days will exceed the less-than-10 microdarcy requirement. We have a larger number of permeability tests planned for the next few months. These will be on the specimens cured and aged for long terms.

5. Compatibility to Drilling Mud

Tests were continued to determine the effect of drilling muds and various additives on the formulations. Zinc oxide, alumina and zirconia recipes were cured and placed in an autoclave with a typical drilling mud. Nine additional additives have been used with the mud with the following results.

<u>Material</u>	<u>Dose</u>	<u>Result*</u>
Polyanionic cellulose	.1-3 lb/bbl	C
Organophilic clay	.5-7 lb/bbl	C
Starch powder filtrate reducer	2-8 lb/bbl	C
Organic thinners	.5-3 lb/bbl	C
Guar gum viscosifier	1-5 lb/bbl	C
Sodium acid pyrophosphate dispersant	.1-.2 lb/bbl	NR
Surface active defoamers	.01-.1 lb/bbl	C
Barite	As required	C
Amines (corrosion inhibitors)	2lb/bbl	I

* C = compatible; NR = Not Recommended; and I = Incompatible.

TABLE V
Shear Bond Strengths

<u>Recipe</u>	<u>Curing Temperature (°C)</u>	<u>Time of Cure</u>	<u>Shear Bond Strength (psi)</u>
ZnO	100	6 Days	1097
	218	3 Days	1200
	218	7 Days	1400
Al ₂ O ₃	218	3 Days	1100
ZrO	218	3 Days	50
ZrO Regenerative	218	14 Days	1250

There are many more additives and probably a half dozen different drilling mud formulations which could be checked. However, we believe that the results shown above and those included in our second technical report are sufficient to show that only a few mud additives are incompatible with our cements. These are the various amines, some phosphates, and an extremely high or low pH, and then only when the cement is in the slurry form. Once set, there are few chemicals that will affect them.

6. Other Properties

Tests to determine the coefficient of expansion, elastic moduli, thermal conductivity, and specific heats will not be run until the 316 to 400°C cement formulations have been established by some of the long-term aging tests. If they are proven sufficiently stable, etc., at these temperatures to warrant the tests, they will then be undertaken. Corrosion tests have been performed on all of the formulations, but only on those cured at the lower temperatures, i.e., those below 200°C. No corrosive effects have been evidenced at these temperatures. The steel nipples which have been used for curing the recipes at the higher temperature of 316°C and above have shown no corrosive reactions. We have not, however, looked at the longer term corrosion possibilities. Earlier tests in 1977 proved that the original SwRI formulations of hydrothermal cements actually inhibited corrosion of steel and gave good protection at least up to the 200°C activation temperature.