CEMENTING OF GEOTHERMAL WELLS

PROGRESS REPORT NO. 6
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Abstract

A coordinated program for the development of improved cements specifically designed for geothermal well applications was started in April 1976. Since that time an assessment of the state of the art of well cementing has been made, a management plan prepared, and research on organic and inorganic cementing materials started. Work accomplished during the period July 1 -September 30, 1977 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, and the University of Rhode Island. A contract with the Southwest Research Institute will be initiated in October. The award of this contract will complete the implementation of the first three elements in the program management plan (problem definition, materials development, and property verification).

Cementing of Geothermal Wells

Progress Report No. 6

July-September 1977

Introduction

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

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

1. Compressive 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 (~ 750°F) to 25% brine solutions, flashing brine, or dry steam.
5. Placement ability, capable of 3 to 4 hr retardation at expected placement temperatures.
6. Compatibility of the cement with drilling mud.
7. Non-corrosive to steel well casing.

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

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

The goals for the overall program are as follows:

1. Preparation of an integrated research and development plan for the investigation of new well-cementing materials specifically designed for geothermal well applications.
2. To provide the technical basis for the development, testing, and practical demonstration of high-temperature cementing materials for geothermal wells.
3. Rapid transfer and implementation of the technology in the private sector.

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

1. Develop well-cementing materials capable of withstanding the environmental conditions in geothermal wells.
2. Perform pilot-scale testing and analysis of the cementing materials at well down-hole conditions.
3. Develop the technology required to mix, pump, and place the cementing material.
4. Demonstrate the process by the cementing of a prototype well.
5. Perform cost analyses to determine the economic viability of the cementing systems under investigation.

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

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

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

This report constitutes the sixth in a series of quarterly reports describing work on the program. Accomplishments during the period July-September 1977 are summarized below. During the quarter work has been performed in Tasks 1, 2, 3, and 7. Work on other tasks will commence in FY 1978 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 downhole test facilities. Testing should be performed in several geothermal environments but the highest priority for near-term (~ 10 yr) application

should be given to medium salinity brines at temperatures up to 400°C (750°F).

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. Implementation of the first three elements in the plan was completed during the current report period. Organizations participating in the program are as follows:

Problem definition, Dowell Division of Dow Chemical Co.

Materials development, Battelle's Columbus Laboratories

Brookhaven National Laboratory

Colorado School of Mines

Dowell Division of Dow Chemical Co.

Pennsylvania State University

Southwest Research Institute

University of Rhode Island

Property verification, National Bureau of Standards

As a means of obtaining technical guidance for the overall program and as an initial step in the technology transfer process, BNL has established a "Geothermal Well Cement Advisory Panel". A list of panel members was given in the previous progress report.² The first meeting of the panel was held at the National Bureau of Standards on May 26, 1977. The second meeting is scheduled for December 7, 1977 at the Union Research Center in Brea, California. Plans have been made to affiliate the panel as a subcommittee of the "American Petroleum Institute".

Task 2. Selection of Well Cementing Materials

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

Polymer Cement

Polymer cements (PC) have been identified as promising well completion materials. Development of these materials is continuing at BNL. To date two monomer formulations, 60 wt % styrene - 40 wt % trimethylolpropane trimethacrylate (TMPTMA) and 50 wt % styrene - 33 wt % acrylonitrile - 17 wt % TMPTMA, have been shown to be durable to geothermal fluids. Both systems can be polymerized using chemical initiators and heat or by chemical initiators and promoters. The former appears suitable for temperatures up to $\sim 150^{\circ}\text{C}$ (302°F) while the latter has given good results up to $\sim 240^{\circ}\text{C}$ (464°F).

During the current report period work with styrene-acrylonitrile formulations containing acrylamide or methacrylamide and crosslinking agents was continued. Three variables: polymer content, and type and concentration of the crosslinking agent were investigated.

Polymer Content

The effect of polymer content on the strength and durability of PC containing a 55 wt % styrene - 35 wt % acrylonitrile - 5 wt % acrylamide - 5 wt % trimethylolpropane trimethacrylate (TMPTMA) monomer mixture was studied. Polymer contents ranging between 12 and 20 wt % were used in conjunction with an aggregate consisting of 70 wt % silica sand - 30 wt % portland cement. Properties measured included water absorption and thermal stability in air and hot brine at 238°C (460°F).

All of the specimens exhibited reductions in strength and increases in absorption after exposure to air and brine at 238°C (460°F) for 30 and 10 days, respectively. Increased polymer content resulted in a decrease in stability.

Crosslinking Agents

The incorporation of crosslinking agents into PC results in significant improvements in thermal stability and durability. During the report period two crosslinking agents, TMPTMA and divinyl benzene (DVB), were used with the styrene-acrylonitrile formulations containing acrylamide or methacrylamide. TMPTMA concentrations of 2.5 wt % and 5 wt % were studied. The DVB concentration was varied from 2.5 wt % to 10 wt %.

The results from these studies indicate that the use of DVB in PC produces composites with greater high temperature brine stability than samples containing TMPTMA. The best results were obtained with samples containing the styrene-acrylonitrile-acrylamide mixture in conjunction with DVB concentrations from 5 wt % to 10 wt %. These samples did not exhibit reductions in strength after exposure to hot brine at 238°C (460°F) for 10 days. Samples prepared without the inclusion of a crosslinking agent and with TMPTMA had strength losses of 50% and ~ 30% respectively, after similar exposures. The tests with DVB are being repeated to determine if the results are reproducible. Longer term tests have also been started.

Aggregate Composition

The durability of PC to geothermal fluids has been found to be highly dependent upon the composition of the aggregate. Materials such as quartz, silica, fly ash, and portland cement have been investigated. All of the materials can be used in composites which have good durability at temperatures

< 218°C (425°F). Above this temperature, only PC materials containing mixtures of silica sand and portland cement have been durable to brine and steam.³

To determine the reason for this effect, infra-red (IR) studies are being performed. In these tests, each of the chemical constituents of Type III portland cement (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , and MgO) have been combined with silica sand and various vinyl-type monomers (MMA, TMPTMA, and styrene) to form PC. IR analyses are being performed on the samples before and after exposure to brine and air at 238°C (460°F) for 30 days. Preliminary results indicate chemical bonding between the CaO and $-\text{CH}_2$ groups in the vinyl monomers.

Evaluation of the control specimens has been completed and work with the specimens after exposure to brine and hot air is in progress. The observations from the control samples are as follows:

1. The absorption band of the $-\text{CH}_2$ groups, for the region 2900-3000 cm^{-1} , of TMPTMA, polymethyl methacrylate (PMMA), and polystyrene in PC containing Type III portland cement and CaO was observed to be much smaller than that of the polymers alone.

2. The IR spectras of TMPTMA, PMMA, and polystyrene in PC's containing $\text{Ca}(\text{OH})_2$, Al_2O_3 , MgO , and SiO_2 were not similar to those when the polymers were used in PC containing Type III portland cement and CaO aggregate.

3. The IR spectras and absorbance ratios for the polymers in PC's containing 66 wt % Type III portland cement were observed to be very similar to those when the polymer was used in PC containing 56 wt % CaO . Calculation of the CaO content in the PC containing the portland cement

indicated a CaO concentration of 56 wt %.

4. The absorption bands for $-\text{CH}_2$ groups at 2998 cm^{-1} for PC containing CaO become smaller as the CaO concentration is increased.

5. The evidence indicates that the CaO reacts chemically with the $-\text{CH}_2$ groups in the vinyl monomers. However, there is no evidence whether the reaction is caused by free CaO or the calcium ion.

IR and mechanical evaluation of PC after exposure to hot air and brine is in progress. Visual examination of the samples indicated cracking of most of the non-portland cement containing materials.

Work has been started to evaluate the use of PC containing polyimides as a possible well cementing materials. A polyimide formed by reacting aromatic diamines with aromatic dianhydrides is currently being studied.

Inorganic Cements

Research on high temperature inorganic cements is in progress at five laboratories. A sixth program will be initiated on October 1, 1977. The status of each program is summarized below.

Colorado School of Mines

G. L. Kalousek, Principal Investigator

Starting date, April 1977

The second quarterly report⁴ for the program is given in Appendix 1.

University of Rhode Island

T. J. Rockett, Principal Investigator

Starting date, July 1977

The first quarterly report⁵ is given in Appendix 2.

Dowell Division of Dow Chemical

D. Free, Principal Investigator

Starting date, July 1977

Battelle's Columbus Laboratories

R. S. Kalyoncu, Principal Investigator

Starting date, September 1977

Pennsylvania State University

D. M. Roy, Principal Investigator

Starting date, September 1977

Southwest Research Institute

D. K. Curtice

Starting date, scheduled to commence October 1977

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 will be conducted.

A testing program that will be a precursor to down-hole evaluation has been started at the National Bureau of Standards. Test equipment is being assembled and tested. Samples of oil well cements used for the completion of geothermal wells have been obtained for use in initial tests.

Task 7. Administrative

During the current report period, three "Monthly Administrative Letters" were submitted to DGE and Quarterly Progress Report No. 5² was issued.

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Appendix 1

Second Quarterly Technical Report

August 1, 1977 to September 30, 1977

BNL/ERDA Contract No. 406003-5

DEVELOPMENT OF CEMENT FOR USE

IN GEOTHERMAL AND DEEP OIL WELLS

Introduction

The research at CSM shows that the hydrothermal products of C-S cements are subject to alterations with increasing temperature, and also affected by introduction of extraneous components such as Al_2O_3 , Na_2O , etc. The alterations caused four effects, some good, some bad, on strength. Of particular interest has been the potentially adverse effect on crystallization and/or re-crystallization of truscottite, the ultimate binder at elevated temperatures in the presence of excess silica. Prolonged curing even at the highest temperature may be required to fully disclose the role of truscottite.

During the past quarter, attention has been directed to other criteria of quality of the cements in addition to strength.

Strength

A type G Portland cement and silica supplied by Halliburton is being tested in comparison with the C_2S -S cements. The type G cement contains 4.1% Al_2O_3 , 5.1% Fe_2O_3 and 2% SO_3 and is being used without any additions except the silica. The W/S used is 0.4 or slightly less to prevent excessive subsidence of the solids in the mold. The βC_2S -S cements are used at W/S of 0.45. The type G cement is being tested at C/(S + A) of 0.98, 0.83, 0.70 and 0.60, the 0.98 being the standard with Halliburton.

The type G cement mixes cured at $150^{\circ}C$ for 24 hours gave higher

strengths than the BC_2S cements, which normally would be attributable to the lower W/S. This is not the explanation. The type G binders were a mixture of αC_2SH , a binder of very low strength, and $CSH(1)$, a binder of superior strength at all $C/(S + A)$ ratios. The binder of the C_2S -S cements was tobermorite. At 250° , 300° and 350° C the dominant phase of the type G cement was xonotlite, generally little to very little truscottite and silica, generally in increasing amount with decreasing $C/(S + A)$ ratio. The compressive strengths ranged between 8,000 and 13,000 psi and independently of the $C/(S + A)$.

To obtain more information on the changes in amounts of truscottite with increasing time of curing, the 0.98, 0.83 and 0.60 $C/(S + A)$ mixes were cured at 350° C for 3, 7 and 14 days. The amount of truscottite increased between 3 and 14 days for the 0.6 $C/(S + A)$ product, remained about the same at 0.83 $C/(S + A)$ and decreased in the 0.98 $C/(S + A)$ product. The amounts of xonotlite and quartz remained unaltered. Some unidentified phase contributed a peak of weak to medium intensity at 3.50A. (Some of these samples are being submitted to Professor Taylor for examination with the Guinier Camera.) It is possible this unidentified phase may contain the Al_2O_3 , Fe_2O_3 or other extraneous component and have some effect on the properties. The small increase in amount of truscottite in the 0.6 $C/(S + A)$ product between 3 and 14 days is indicative of a very slow rate of truscottite formation from xonotlite, even at 350° C.

Attainment of Equilibrium of C_2S -S Cements

Tests on 0.6 to 1.0 C/S pastes to determine attainment of equilibrium in the shortest time are continuing. The 1.0 C/S mixes reached equilibrium, xonotlite only with no reactants, in short time, less than

7 days at 175⁰ C and less than 1 day at 350⁰ C. The 0.83 C/S mix yields the equilibrium products, xonotlite and gyrolite, between 7 and 28 days at 200⁰ C, and xonotlite and truscottite between 7 and 28 days at 250⁰ C using nominally pure BC₂S and silica. The 0.6 C/S product should yield pure truscottite at about 225⁰ C, but even at 350⁰ C for 14 days some other unidentified phase appears to persist with the truscottite. Mixes with added Al₂O₃ yield even more complex results. (A few of the 0.6 C/S products will be sent to Professor Taylor for evaluation.) The need of developing unequivocal results of crystallization of truscottite is urgent because this is the ultimate phase to coexist with excess silica at elevated temperatures.

Volume Changes

Test procedures and necessary equipment for determining volume change have been developed and obtained, respectively. The tests will provide results on volume change during (1) phase transformation, (2) deliberately induced expansion, (3) saline water attack, and (4) drying shrinkage. The specimens at 0.6 to 1.0 C/(S + A) are 1 x 1 x 5 inch bars precured at 150⁰ C for 24 hours, conditioned in 73⁰ F water and measured for initial length with a comparator. The specimens will be cured successively at 175⁰, 250⁰ and 300⁰ C for 7 days and after each curing, length measurements will be made. Specimens, 1/2 x 1/2 x 1.8 inch in size, will be simultaneously processed in the event it becomes desirable to determine the product for phase change. These small specimens will probably supply useful information on saline water attack in the event such attack does not cause expansion. (The deliberate induction of expansion is planned for later tests.)

Cement-Wallrock/Steel Casing Bond

It has been decided to measure bond strengths using a specimen consisting of a 2 inch D. x 1 inch steel ring with a 1 inch D. rock specimen centered in the ring and surrounded by the cement. The assembly would be precured at 150° C and then cured at higher temperatures up to 350° C in initial tests. The rock specimen, which is 2 inches high, will be loaded to points of initial and final failures. The improved loads will be calculated as bond strength. The design of the specimen assembly and test procedure was done with the intention of studying the effects of residual drilling mud at the interfaces on the bond strengths. A 1 inch diameter steel tubing will replace the rock specimen in the determination of the steel casing-cement bond.

In consultation with the people in the Earth Mechanics Institute, Dr. Romberger in Geology at CSM, and Dustin Free of Dowell Division of Dow Chemical U.S.A., the following rocks were selected tentatively for present tests: basalt, rhyolite, quartz (or sandstone), granite, limestone (or dolomite), shale and siltstone. The granite, sandstone and shale were immediately available and have been fabricated into test specimens. The available shale was too brittle for coring. The available rocks have also been reduced to a minus 100 mesh sieve to be used with the cement for compressive strength measurements. It is not possible to predict if time will permit testing of all the rocks.

Summary

The studies on the effect of truscottite on strength using Portland and C₂S cements is progressing slowly due to the apparently required prolonged curing. The formation of α C₂SH and CSH(1) as initial binders in the type G cements which transform essentially to xonotlite of very

high strength adds a new facet to the research. Our earlier research on $\beta\text{C}_2\text{S}$ -S cements showed clearly that transformation to xonotlite is accompanied by serious strength retrogression. The question, of course, arises now about the effect of the Al_2O_3 , Fe_2O_3 , SO_3 and other minor cement constituents in the cement.

George L. Kalanick

Appendix 2

BNL Contract 418691-S

PHOSPHATE BONDED GLASS
CEMENTS FOR GEOTHERMAL WELLS

Technical Report No. 1
July to September, 1977

from

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University of Rhode Island
Kingston, Rhode Island

to

Process Technology Division
Department of Applied Science
Brookhaven National Laboratory
Upton, New York, 11973

Contributors: T. J. Rockett
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I. Introduction

This report covers the work done on the contract entitled, "Phosphate Bonded Glass Cements" during the period of July 1, 1977 to October 1, 1977. During this period, experimental work was begun on several alumina refractory cements, using both phosphate solutions and waters as the reactive liquid. Literature surveys were also begun on phosphate bonding and on cement slurry rheology.

II. Experimental Results:

A. Hydraulic Alumina Cements:

All phosphate cementing involves the leaching or dissolution of various ions from a cement powder into a phosphate liquid.¹ The dissolved constituent interacts with the phosphate liquid to yield a crystalline or amorphous cement phase. These cements are known as phosphate cements, oxyphosphate cements, acid phosphate cements and alumina phosphate cements.² Even the so-called silicate cements are more properly classified as phosphate cements because the setting results from the leaching of calcium and aluminum ions from a silicate glass with subsequent reaction to form calcium and aluminum phosphates.³ With the exception of the zinc phosphate cements, which are not stable at elevated temperatures, the aluminum ion is a key to phosphate cementing. For this reason, our investigation of possible geothermal well cements has begun with an investigation of alumina refractory cements.

Table 1 lists the setting properties of a high alumina "castable" refractory cement. This material was examined because it is known to form a cementitious bond at low temperature

TABLE 1 - SETTING TIME OF A HIGH ALUMINA
REFRACTORY CEMENT

	<u>Powder</u>	<u>Liquid</u>	<u>Powder/Liquid</u>	<u>Temp.</u>	<u>Condition</u>	<u>Setting Time</u>
1)	EA 139	H ₂ O	5	25°C		80 hrs.
2)	EA 139	H ₂ O	5	60°C	100% Humidity	7.5 hrs.
3)	EA 139	H ₂ O	5	60°C	100% Humidity	5.75 hrs.
4)	EA 139	H ₂ O	5	60°C	Dry	4.25 hrs.
5)	EA 139	H ₂ O	5	100°C	100% Humidity	2.5 hrs.
6)	EA 139	H ₂ O	5	100°C	Dry	2.0 hrs.
7)	EA 139	H ₂ O	5	100°C	(Sealed)	724 hrs.

which is stable to temperatures in excess of 1000°C. The material was also used to determine a powder liquid ratio which would result in a pumpable slurry for emplacement. The powder liquid ratio of 5 which was chosen for the experiments is a weight ratio. Hence a typical test sample was made by mixing 30 grams cement powder with six ml. of water.

The setting times were determined using a 1 pound gilmore needle. When no indentation in the cement surface is observed the cement is deemed to have set. Determinations were made every 15 minutes after the approximate set time was established. Sample 7 represents a mixture which was sealed in a polypropylene bottle and heated to prevent water loss. With all water retained, the sample did not set in twenty-four hours. It appears that some dehydration must take place in order to promote setting. The implications of this finding to geothermal well completion will be discussed below.

X-ray diffraction analysis showed the cement to be a two phase mixture of α -alumina and potassium β "-alumina. The beta alumina has a composition of KAl_5O_8 i.e. a molar ratio of 1 K_2O to 5 Al_2O_3 ⁴. The α -alumina is present as a filler material while the β "-alumina serves as the reactive component. On mixing, the pH increases to about 10. K^+ is leached from the compound and the basic solution breaks down the β "-alumina framework. Subsequent reaction probably forms a potassium aluminum hydrate gel phase which is the cementing phase.

There are several different types of hydraulic alumina cements. They have been classified by Briebach on the basis of

their alumina to lime ratio.⁵ His classification is given in Table II and we have added the phosphate bond cements to the group. Next to portland cement, the calcium aluminate cements are the most widely used cements. Castable cements are made up of a mixture of pure alumina (60 to 80% filler) and a reactive alumina cement powder. The reactive cement may be one of the calcia-alumina cements of Table II or an alumina phase with other cations.

B. Phosphate Bonded Cements:

That alumina will form a bond with phosphoric acid that becomes permanent on heating is well known.⁶ Usually some degree of heating is required to form the bond. It is also known that other oxides such as chromia, zirconia and perhaps silica will also form such a bond.

Table III shows the results of some experiment conducted on various types of alumina and one type of silica. The powder/liquid ratio was chosen to yield a mass which could be pumped. The phosphate liquids become increasingly viscous with increased P_2O_5 content and there the powder liquid ratio must be reduced to yield a flowable mass. Also, the powder liquid ratio for alumina and silica is drastically different indicating a strong adsorption of the solution on the alumina grains. No cements were formed with α - Al_2O_3 or silica (-quartz) at 200°F. Using γ -alumina, some very strong bodies were formed with the 51% and 68% phosphoric acid solutions. The difference in cement forming between α and γ is believed to be due to the metastability of γ .

TABLE II. CLASSIFICATION OF ALUMINA CEMENTS

<u>Approximate Composition</u>				<u>Al₂O₃/CaO</u>	<u>Liquid</u>	<u>Names</u>
Al ₂ O ₃ :CaO:SiO ₂ :Other						
10	60	22	8	0.1	Water	Rapid fired portlant cement. Blast furnace cement.
40	38	7	15	1.1	Water	High alumina cement. Tricalcium aluminate cement.
60	35	5	--	- 2.0	Water	High alumina cement. Low iron alumina cements.
80	20	-	--	3-5	Water	White high alumina cement. Alumina refractory cement. Fused alumina cast-ables.
100	--	-	--	N/A	Phosphate Solution	Aluminophosphate cement. Phosphate bonded alumina

TABLE III. SETTING TIME OF PHOSPHATE BONDED CEMENTS AT 200°F

Test	Powder (average particle size)	Liquid (w/o H ₃ PO ₄)	Powder/Liquid (wt)	Humidity	Results
1.	α-Al ₂ O ₃ 50μ	29	1.0	100%	No setting. Dry Powder.
2.	α-Al ₂ O ₃ 50μ	51	0.9	100%	No setting. Wet Cake.
3.	α-Al ₂ O ₃ 50μ	68	0.9	100%	No setting. Wet Cake.
4.	α-Al ₂ O ₃ 1μ	29	0.6	100%	No setting. Dry Powder.
5.	α-Al ₂ O ₃ 1μ	51	0.55	100%	No setting. Dry Powder.
6.	α-Al ₂ O ₃ 1μ	68	0.5	100%	No setting. Wet Cake.
7.	γ-Al ₂ O ₃ 0.05μ	29	0.3	100%	Surface set - 12 hours
8.	γ-Al ₂ O ₃ 0.05μ	51	0.3	100%	Solid cement in 12 hours. Full of bubble.
9.	γ-Al ₂ O ₃ 0.05μ	68	0.28	100%	Solid cement - hydroscopic.
10.	γ-Fired @ 900°C	29	0.3	100%	Same as 7.
11.	γ-Fired @ 900°C	51	0.3	100%	Same as 8.
12.	γ-Fired @ 900°C	68	0.28	100%	Same as 9.
13.	γ-Al ₂ O ₃ 0.05μ	29	0.3	Sealed	No setting - 46 hours.
14.	γ-Al ₂ O ₃ 0.05μ	51	0.3	Sealed	No setting- 46 hours.
15.	γ-Al ₂ O ₃ 0.05μ	68	0.28	Sealed	No setting - 46 hours.
16.	SiO ₂ 25μ	29	3.0	100%	Dry cake - no setting.
17.	SiO ₂ 25μ	51	2.5	100%	Dry cake - no setting.
18.	SiO ₂ 25μ	68	2.0	100%	Moist cake - some plasticity

The α -phase is stable at room temperature and less subject to attack by phosphoric acid. Experiments to convert γ to α at 900°C were not successful. X-ray examination of the γ material before firing showed that it contained at least 50 percent of α -alumina. These cements were submerged in water for one hundred hours. They did not break down or dissolve but did show a weight loss of 2 percent. They were somewhat chalky after soaking and appeared to have lost some strength.

The successful cements contained a large proportion of bubbles distributed throughout the set mass. We believe the bubbles result from water vaporization. The phosphate liquids are hygroscopic and equilibrate with the PH_2O in the test chamber. As PO_4^{3-} groups react with alumina, water is given off by the solution. These observations raised the question of the role of water loss in setting. As mentioned above, no setting was observed in the hydraulic aluminate cements unless some water loss was observed. Experiments 13 to 15 confirmed this phenomenon in phosphate bonded aluminas. The implication of these findings to the cementing of geothermal wells is important. Several well known phosphate cements would be useless in the geothermal environment. Up to 46 hours, no cements were observed to form in sealed polypropylene bottles.

Some insight into the behavior of these phosphate - alumina mixtures can be obtained by referring to the phase diagram for the system shown in figure 1.⁷

The phase diagram is divided into three areas:

(1) totally solid phase assemblages; (2) mixtures of solids and liquid; and (3) an all liquid region. If a liquid of composition A is mixed with a soluble form of alumina the composition of the liquid will shift as shown on figure 1. At point "a", some of the nono-hydrate will begin to form. This will lead to crystal growth on the surface of the undissolved alumina grains and it will also cause the liquid phase to become rich in H_2O . Subsequent water loss or vaporization at high temperature could result. If the reaction continued, more crystallization would result in a total solidification of the mass. (Point C-Figure 1)

The dissolution rates however are extremely slow even with metastable γ -alumina. Equilibrium times for saturation of these liquids at $60^\circ C$ is between six months and 1 year.

Therefore setting of a phosphate cement by this mechanism at room temperature is probably impossible. However, if water loss is combined with dissolution of alumina, the all solid state can be reached by dissolving half as much alumina. The kinetics of a closed system at temperatures higher than $60^\circ C$ is not known. Since these reactions are critical to phosphate bonding under geothermal conditions, our future plans include an investigation of this reaction rate at $200^\circ C$.

C. Powder-liquid ratios and Pumpability:

The restriction that the cements for well completion be pumpable places severe limitations on phosphate cements. One estimate for portland type cements is that there must be 40 weight percent water in the slurry for pumpability.⁸ In order to test materials at consistencies which would be within the range of usability we have begun determining viscosities of slurries as a function of powder liquid ratio.

After some preliminary work with vibrating Zahn cups it was decided that more accurate data could be obtained using a rotating spindle viscometer. A series of tests will be completed to fix the viscosity of various powder/liquid ratios for a range of phosphate liquids.

III. Future Plans

- Work will continue on the setting of alumina with phosphate liquids under sealed conditions.
- Experiments will be conducted to determine the 200°C isotherm in the System $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ under sealed conditions to establish the optimum liquid composition range for aluminophosphate bonding.
- Powder-liquid ratio studies versus viscosity will be completed for various phosphate liquids using α -alumina as a filler.
- The cementing of high alumina glasses will be investigated. Work will begin on calcium-alumino-silicate glasses.

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