CEMENTING OF GEOTHERMAL WELLS

PROGRESS REPORT NO. 10
JULY - SEPTEMBER 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 July 1 - September 30, 1978 is described in the current report.

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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, Dowell, Pennsylvania State University, Southwest Research Institute, University of Rhode Island and the National Bureau of Standards. Experimental work has been completed at the Colorado School of Mines and a final report is being prepared. Samples of β -dicalcium silicate-silica cement developed in this program have been submitted for additional evaluation at Dowell and the National Bureau of Standards.

Phase II of Dowell's program is continuing. The initial screening portion of this work has identified several promising systems that will undergo more rigorous testing. Dynamic brine exposure testing of several systems has been initiated at the East Mesa Geothermal Test Facility. Testing at the Niland test site is scheduled to start soon.

Property verification tests on cements produced in the materials development phase of the program were initiated at the Bureau of Standards. Preliminary data are available for five cements exposed for 176 hr to water at a temperature of 195°C. Three of the cements exhibited strength losses during the test. An aluminum hydroxide cement and a polymer cement showed slight increases in strength after the exposure. These and longer-term data will be utilized in the selection of a material for use in the remedial cementing of a hot dry rock well at the Los Alamos Scientific Laboratory. A recommendation for a material will be made in December. The remedial cementing is scheduled for January 1979. If implemented, this will represent the first down-hole test of a cement developed in the program.

Cementing of Geothermal Wells

Progress Report No. 10

July - September 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 used at that time deteriorated 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 were 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 tenth in a series of quarterly reports describing work on the program. Accomplishments during the period July - September 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 program 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. All segments of the geothermal industry attend the meetings. The first meeting of the Task Group was held in Tulsa, Oklahoma in June 1978. The second meeting is scheduled for January 24-25, 1979 at the Society of Petroleum Engineers of AIME Meeting in Houston, Texas.

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 crosslinked mixtures of styrene (St), acrylonitrile (ACN) and acrylamide (Aa).

Samples consisting of a mixture of 50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% divinyl benzene (DVB) and an aggregate containing 70 wt% sand - 30 wt% cement were sent to the National Bureau of Standards for use in property evaluation tests. This work is described in Task 3. The compressive strengths of the control specimens averaged $\sim 23,000$ psi.

Equipment to measure the viscosity changes in PC mixtures at high temperatures and pressures has been assembled and tests are in progress. These data are required before pumpability tests can be initiated. In order to insure pumpability, it is essential that the viscosity of the mixture remains essentially constant for ~ 4 hr at the anticipated placement temperature and pressure.

The flow sheet for the high pressure system being used in these tests is shown in Figure 1. PC samples, in ~ 50 g quantities, are placed in the 100 cc volume pressure vessel and the vessel is subsequently subjected to the desired temperature and pressure conditions for a predetermined period of time. At the end of this time, the pressure is vented and the vessel quenched in cool water to lower the temperature. The fluidity of the PC and the percentage of monomer converted to polymer are then determined.

Figure 1. High pressure equipment being utilized in preliminary tests to measure the pumpability of polymer cement formulations.

Figure 2. The effect of the substitution of C_3S for an amount of type III Portland cement on swelling diameter changes and compressive strength of PC after exposure to brine.

To date, preliminary tests have been performed at temperatures of 75°C and pressures up to 3000 psi. These data will be summarized in the next report.

2.2 Aggregate Composition

During a study to determine the effects of calcium compounds of cement on the thermal stability of vinyl-type polymers, it became apparent from Differential Scanning Calorimeter (DSC) studies that tricalcium silicate (C_3S) had a far greater effect than other calcium compounds.² It was also determined that the residual free lime content of the C_3S must be kept below 2 wt% because of the physical expansion of the $Ca(OH)_2$ products which are formed due to the chemical reaction between free lime and water.³

During this report period, the effect of C_3S on the thermal stability of vinyl-type polymers was clarified further by mechanical property measurements. In this study the free lime content in the C_3S was maintained in the region 1.5 to 1.8 wt%. The first PC samples tested in this series contained various concentrations of C_3S which were substituted for a portion of the portland cement filler. Diameter changes and the compressive strengths were determined for the 3.13-cm-diam x 6.25-cm-long samples after exposure for 30 days to a 25% brine solution at 238°C.

The results from this series of tests are shown in Figure 2. The data indicate that the dimensional stability and compressive strength after brine exposure can be increased by substituting C_3S for a portion of the cement filler. The compressive strengths before and after exposure to brine of PC specimens, in which all of its 17 wt% Type III portland cement was replaced by C_3S , were 18,210 psi and 16,600 psi, respectively.

This decrease, ~ 9%, in strength was also far less than that obtained from PC containing 17 wt% C_2S .³

An estimate of the most suitable amount of C_3S to be used was made by a second series of mechanical property tests. PC specimens containing 0, 5, 10, 20, and 38 wt% of C_3S as a weight proportion of the aggregate, were prepared by thermal polymerization in a dry oven at 85°C for 24 hr, using 2 wt% benzoyl peroxide as an initiator. The results of compressive strength tests before and after exposure for 30 days to 25% brine at 238°C were used to determine the best composition. These results, shown in Figure 3, indicated that PC containing 20 wt% C_3S had the highest strength when compared with other compositions.

The compressive strength values obtained from the first mechanical evaluation were found to yield a curve similar to that obtained from the relationship between the compressive strength and the C_3S content. This indicates that the effect of cement on the thermal stability of vinyl-type polymers is due to the C_3S which occurs as a major constituent in Type III portland cement. The C_3S content of Type III portland cement used in this study was about 52 wt%. The results also suggest that the decreasing trend in compressive strength of PC after exposure to brine may be controlled by the addition of C_3S ; namely, the decrease in strength of PC containing 38 wt% C_3S is only about 0.4%.

A possible explanation for the improved stability due to the presence of C_3S may be the hydration products of C_3S formed when the compound is subjected to hot brine. Therefore, an experiment was performed using infrared (IR) spectroscopic analysis to determine if hydration products are formed in the PC after exposure to brine. These results will be

Figure 3. Relationship between compressive strength and C_3S content of PC.

described in a later section which will also present IR analysis data for PC samples which were prepared by the mixing of condensation and addition-type polymers with sand and C_3S as aggregate.

In the IR studies, the effects of C_3S on the thermal stability of phenol-formaldehyde resin (PFR), epoxy resin and furan resin, prepared by other polymerization methods such as hydrogen transfer and condensation polymerization, were analyzed. DSC was also used in these experiments.

The solids content of PFR prepared by the condensation reaction of phenol and formaldehyde in a water solution was in the region of 61 to 63%. The polymerization was performed under the following conditions: 24 hr at $60^{\circ}C$, 10 hr at $80^{\circ}C$ and 24 hr at $150^{\circ}C$.

The epoxy resin used in this study was a diglycidal ether of bisphenol A. The polymerization was carried out under the following conditions: 24 hr at $85^{\circ}C$ in hot air.

The polymerization of furan resin was performed by heating for 24 hr at $85^{\circ}C$ and 24 hr at $130^{\circ}C$.

The DSC thermograms for these resins are shown in Figure 4. Samples identified a and b show the thermograms of bulk PFR and PFR containing 42 wt% C_3S , respectively. The broad endothermic peaks at 105° and $115^{\circ}C$ are probably a result of the influence of the physically combined water and other low molecular products.⁴ The thermogram of bulk PFR in a nitrogen atmosphere is characterized by the endo and exothermic peaks at $190^{\circ}C$, $260^{\circ}C$, and $344^{\circ}C$. For the PFR containing C_3S , it is interesting to note that the thermogram does not exhibit prominent endo and exothermic peaks at these or other temperatures except for the endothermal effect at about $450^{\circ}C$. This interesting fact is considered to occur due to the chemical

Figure 4. Differential scanning calorimeter thermograms (DSC): a, 100 wt% PFR; b, 58 wt% PFR + 42 wt% C₃S; c, 100 wt% epoxy resin; d, 58 wt% epoxy resin + 42 wt% C₃S; e, 100 wt% furan resin; f, 58 wt% furan resin + 42 wt% C₃S.

reaction between C_3S , water and functional groups in the PFR.

In order to monitor the reaction occurring between the C_3S and the PFR, the temperature was measured during the mixing of the PFR with Type III portland cement. These results are shown in Figure 5. The mixtures of 50 wt% PFR and 50 wt% cement showed a reaction temperature of $44^{\circ}C$ in about 1 minute and 40 seconds. A decrease in the amount of cement used extends the length of time to the maximum reaction temperature, as shown in the figure. This appears to be due solely to the chemical reaction between the PFR and cement since X-ray Diffraction studies did not indicate the presence of hydration products. Consequently, the onset temperature (T_d) of the first endothermal effect of a new material produced by the reaction of 58 wt% PFR and 42 wt% C_3S was increased from about $160^{\circ}C$ for bulk PFR to about $300^{\circ}C$ by the addition of C_3S .

On the other hand, the thermogram of bulk epoxy resin showed endothermic peaks at 136° , 225° , 283° , and $363^{\circ}C$ and an exothermic peak at $343^{\circ}C$. The thermogram of epoxy resin containing 42 wt% C_3S produced a curve similar to the one obtained for bulk epoxy resin. This seems to indicate that an interaction between the C_3S and the epoxy resin does not occur.

Furan resin samples produced results similar to those obtained with the epoxy resin samples. The thermogram of bulk furan resin did not exhibit a noticeable difference from that of the resin combined with C_3S .

In order to obtain further information about the chemical reaction between C_3S and PFR, IR analysis was performed by using KBr pellets prepared by mixing 200 mg of KBr and ~ 3 mg to 4 mg of the PC samples crushed to under 0.104 mm. Figure 6 shows IR spectras of PFR and epoxy resin samples.

Figure 5. Reaction temperature vs. time curves of the PFR-cement reaction.

Figure 6. Infrared spectra of PFR-C₃S and epoxy-C₃S samples.

Analyzing the IR spectra of bulk PFR, the absorption band at 3350 cm^{-1} is a stretching vibration of bonded O-H groups. A stretching vibration of the C-OH groups in the polymer is apparent at 1200 cm^{-1} . The bands at 1350 cm^{-1} may be due to the bending vibration of O-H groups. The absorption bands at 2900 cm^{-1} and 1480 cm^{-1} are a result of the valency and deformation vibration of the CH_2 groups. The absorption band at 1602 cm^{-1} may be due to skeletal n-plane vibration of the benzene ring.

For the PFR containing C_3S , the most significant change in the spectra is the disappearance of bending vibration of the O-H groups at 1350 cm^{-1} by the addition of C_3S . The chemical meaning of this phenomenon is considered to be a reaction between the highly polar hydroxyl group and the C_3S . However, there is no evidence whether the bond is from the hydrogen or the hydration bonds of C_3S .

For the epoxy resin specimens, the IR spectras of samples containing C_3S were essentially the same as that of the bulk epoxy resin.

The conclusions from the results described above are as follows. Previously reported IR data³ for vinyl-type PC containing C_3S indicate that the absorption band of the $-\text{CH}_2-$ group in the vinyl-group for the region $3020\text{--}2900\text{ cm}^{-1}$ is much smaller than that of bulk vinyl-polymers. This suggests that the chemical interaction between the $-\text{CH}_2-$ group and the C_3S is greatly enhanced by the addition of calcium compounds. However, for the $-\text{CH}_2-$ group existing in an epoxy or furan resin molecule, decreasing transmittance of the absorption bands of these groups in the region of $3000\text{--}2800\text{ cm}^{-1}$ did not result from the addition of C_3S . Thus, it is assumed that the C_3S reacts with only $-\text{CH}_2-$ groups that takes part in radical polymerization.

The fact that PC containing C_3S exhibits higher strength after exposure to brine than non- C_3S materials may also be due to the hydration of the C_3S . PC specimens, 2.2-cm-diam x 4.4-cm-long, of the following compositions were prepared to investigate this:

PC-1, 24 wt% PFR-61 wt% sand-15 wt% C_3S

PC-2, 25 wt% Epoxy-60 wt% sand-15 wt% C_3S

PC-3, 13 wt% MMA-70 wt% sand-17 wt% C_3S

PC-4, 13 wt% (55 wt% St-36% ACN-9% TMPTMA)-70 wt% sand-17 wt% C_3S

IR analyses of the samples were made after exposure for 10 days to 25% brine at 238^oC. The samples were sectioned as shown in Figure 7, and the samples were then crushed to < 0.104 mm for IR analysis.

Results are shown in Figures 7-10. Figure 7 shows the IR spectra for different sections of PFR samples. The characteristic absorption bands of PFR concrete before exposure to brine are the stretching vibration of Si-O groups at $\sim 1040\text{ cm}^{-1}$ and at $\sim 780\text{ cm}^{-1}$. In PFR concrete containing C_3S , after exposure to brine, the degree of hydration of C_3S can be detected by the bands of $Ca(OH)_2$ at $\sim 1440\text{ cm}^{-1}$, the shoulder at $\sim 1200\text{ cm}^{-1}$, and the bands at $\sim 950\text{ cm}^{-1}$. The IR spectra also illustrate that hydrated calcium silicate was produced. It is also apparent that the $Ca(OH)_2$ bands at $\sim 1440\text{ cm}^{-1}$ increase with progression from the center of the sample toward the outside. PFR concrete after polymerization is a porous material having a continuous pore structure compared with the independent pore system of PC specimens produced by addition polymerization. Therefore, it is suggested that when these specimens were exposed to brine, water permeated to the inside of the samples resulting in the hydration of the C_3S . However, rearrangement

Figure 7. Infrared spectra of different sections of PFR concrete after exposure for 10 days to 25% brine at 238°C.

of polymer molecules which takes place due to chemical attack by hot brine was not confirmed from the IR spectra.

Figure 8 shows the IR spectra from various sections of epoxy resin samples. The spectra of epoxy resin concrete after exposure to brine indicate a new band at $\sim 1570 \text{ cm}^{-1}$, probably due to rearrangement of polymer molecules, and bands at $\sim 1440 \text{ cm}^{-1}$, $\sim 1200 \text{ cm}^{-1}$ and $\sim 960 \text{ cm}^{-1}$, which may be due to the formation of hydrates of C_3S . However, there is no evidence how this rearrangement occurs.

Figure 9 shows the IR spectra of different sections of PMMA specimens. Sample No. C, near the surface of the PC, was observed to have absorption bands at $\sim 1200 \text{ cm}^{-1}$ and at $\sim 960 \text{ cm}^{-1}$ due to the hydration of C_3S . However, the absorption bands of hydrated CS from the surface of PMMA concrete towards the center illustrates a rapidly decreasing trend. A possible cause for this is that the porous structure of PMMA concrete consists of closed pores. The degree of hydration of C_3S near the surface of samples is high but, the low permeability of the surface prevents the movement of hot brine to the center of the PC specimens. From the new absorption bands at $\sim 1530 \text{ cm}^{-1}$ and at $\sim 1400 \text{ cm}^{-1}$, the IR spectra also indicate that carbonylate groups ($-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$) of PMMA were converted to carboxylate ions ($-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$) by the highly concentrated base and high temperature. On the other hand, the $-\text{CH}_2-$ group of PMMA concrete showed a stable structure as is evident from data given in Table 1.

Figure 10 shows the IR spectra for different sections of polymer concrete containing the St-ACN-TMPTMA system. As is shown in Figure 10, a section near the surface (sample No. C) after exposure to brine shows evidence at $\sim 1200 \text{ cm}^{-1}$ and $\sim 960 \text{ cm}^{-1}$ of the hydration of C_3S .

Figure 8. Infrared spectra of different sections of epoxy concrete after exposure for 10 days to 25% brine at 238°C.

Figure 9. Infrared spectra of different sections of PMMA concrete after exposure for 10 days to 25% brine at 238°C.

Figure 10. Infrared spectra of different sections of ST-ACN-TMPTMA co-polymer concrete after exposure for 10 days to 25% brine at 238°C.

These absorption bands also illustrate that the amount of hydrated C_3S decreases towards the center of the PC. The results are almost the same as those obtained from the IR spectra of PMMA concrete. Furthermore, it can be seen from the size of the bands at $\sim 1200\text{ cm}^{-1}$ and $\sim 960\text{ cm}^{-1}$, that the degree of hydration in sections at the middle and center of the specimens is very slight. The polymer concrete after exposure to brine was also observed to show bands of carboxylate ion at $\sim 1530\text{ cm}^{-1}$ and at $\sim 1400\text{ cm}^{-1}$. These bands are assumed to be from the transfer of TMPTMA molecules which are used for crosslinking.

In Table 1 the stability towards thermal degradation of $-CH_2-$ groups, in the range of $2950\text{ to }2900\text{ cm}^{-1}$, in condensation and addition-type polymers, is illustrated by values for absorbance per unit weight of the samples. As shown in the table, the absorbance of the control and various sections of vinyl addition-type polymer concretes was essentially constant. The absorbance of condensation-type polymer concretes did not remain constant. From this interesting fact, it appears that C_3S interacts only with $-CH_2-$ groups in the main chain of vinyl addition-type polymers.

The changes in weight and diameter of these samples after exposure to brine are shown in Table 2. The increase in weight of PFR and co-polymer concretes is believed to be due to the hydrated C_3S produced by the hot water. Swelling diameter changes are also very slight. It is assumed that the weight of the PMMA concrete is due to a balance between a slight degradation of the polymer and the hydration of the C_3S . The epoxy resin concrete disintegrated completely due to a large expansion of the polymer.

Table 1

Absorbance of $-\text{CH}_2-$ Groups from Different Sections of Samples of Condensation - and Addition-Type Polymer Concretes Containing C_3S After Exposure for 10 Days in 25% Brine at 238°C

Different Sections	Absorbance mg. in disk of $-\text{CH}_2-$ group ($\times 10^{-1}$)			
	PMMA (2950 cm^{-1})	Copolymer ^a (2900 cm^{-1})	PFR (2900 cm^{-1})	Epoxy (2900 cm^{-1})
Control	0.064	0.044	0.012	0.177
A	0.063	0.030	0.021	0.300
B	0.066	0.030	0.030	0.495
C	0.060	0.039	0.016	0.270

^aCopolymer: 55 wt% St-36 wt% ACN-9 wt% TMPTMA

Table 2

Stability of Condensation and Addition-Type Polymer Concretes Containing C_3S after Exposure for 10 Days to 25% Brine at 238°C

Composition ^a	Change in	
	Weight (%)	Diameter (%)
24 wt% PFR-61 wt% S-15 wt% C_3S	+ 2.96	+ 0.54
25 wt% Epoxy-60 wt% S-15 wt% C_3S	- 11.46	-- ^b
13 wt% MMA-70 wt% S-17 wt% C_3S	0.00	+ 1.01
13 wt% P-70 wt% S-17 wt% C_3S	+ 1.49	+ 0.60

a. P = 55 wt% styrene-36 wt% acrylonitrile-9 wt% TMPTMA;
S = 50 wt% No. 16 sand-25 wt% No. 30 sand-25 wt%
No. 100 sand.

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

2.3 Inorganic Cements

Research on high temperature inorganic cements has been completed at one institution and is in progress at five others. A short summary of the most recent progress report for each program is given below. The full report is included in the Appendix.

Colorado School of Mines

G.L. Kalousek, Principal Investigator

Starting date, April 1977.

Dr. Kalousek completed the experimental phase of his program on September 30, 1978. A 25-lb sample of β C₂S-silica cement has been sent to NBS for property evaluation. Additional samples have been sent to Dowell for use in permeability and thickening time measurements. A final report for the research effort will be prepared by January 31, 1979.

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 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 materials and systems developed in Phase II.

Phase II of Dowell's DOE contract has continued this quarter with work to develop a new and improved geothermal cementing system as well as continued effort to build a data base of information on systems already in use. The initial screening program has already identified several promising systems that will undergo more rigorous testing.

All of the thickening time tests have been completed for the systems entered into the initial screening program. Of those passing that test, a high percentage have successfully met the minimum short term compressive strength requirements. Over the long term, however, many of these systems are expected to fail. Permeability evaluation has also been completed. Next quarter, the crucial bonding and expansion tests will be initiated.

Research to evaluate the effect of heavy (Salton Sea) brines on silica stabilized portland cement systems continued this quarter. It has been determined that the particle size of the silica is an extremely important factor in a cement's ability to withstand degradation when exposed to geothermal conditions. Silica within the particle size range of 3 to 10 μm is optimum for stabilization due to rate of solubility considerations. Also, as a general rule, coarser grind cements are easier to stabilize than fine grinds.

Dynamic brine exposure testing of cement systems deemed to have promise has begun at the East Mesa Test Facility near San Diego, California. Testing at the Nilands, California, test site is scheduled to start soon. Also, the laboratory geothermal simulator, D-BETA, is nearing completion and will be operational in mid-November. The dynamic tests are very rigorous and should serve as a very good indicator of a cement's suitability for use in a geothermal environment.

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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.

During the report period compressive strength and cement-to-metal casing bond strength evaluations of cementing compositions cured for 1 day, 7 days, and 28 days at 232°C and saturated steam pressure were continued. Also thickening time measurements on several compositions with 30% Class J oil well cement were made. The experiments were carried out both at room temperature and in the hot can assembly. The strength measurements were carried out under these two different conditions to emphasize the importance of high temperatures and steam pressures (which the cementing compositions are subjected to at the geothermal well site) on the mechanical properties of the cements. As the data presented indicate, the 24-hour compressive strengths of all the cementing compositions studied (either measured at room temperature or in the hot can) exceed the required minimum value of 1000 psi. Very little or no deterioration of strength is observed upon longer time exposures to high

temperatures and steam pressures as indicated by the strength values of samples cured for 7 and 28 days.

Reduction of cement content from 40 to 30% also did not noticeably affect the strength values, indicating that the additives used develop certain cementing qualities under the curing conditions. Increase in the thickening times, however, was noticed with compositions containing 30% Class J oil well cement compared to those with 40% Class J cement. Cement-to-metal bond strengths continue to be very high regardless of the test conditions (room temperature or hot can assembly) indicating that casing-to-cement interface would not present a problem to efficiency or the life of the geothermal well.

Pennsylvania State University

D.M. Roy, Principal Investigator

Starting date, September 1977

The objectives of this research are to develop new high temperature cementing materials for geothermal wells. The work involves investigation of compositions which lie dominantly within the systems $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$.

During this past quarter approximately 30 runs have been completed and other long term runs are in progress to establish equilibrium phase relations and to determine the properties of modified Class J and calcium-aluminate cements reacted at high temperatures and pressures. X-ray diffraction/phase equilibria studies within the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ have concentrated on delineating phase relations near the join: xonotlite-chrysotile. Differences in the viscosities of slurries were related to systematic differences in total composition (e.g. cement + Al_2O_3 , MgO, or retarding additives) and different forms of added SiO_2 (tripoli,

minasil, quartz sizes). Microhardness as an indicator of strength was measured on 36, 63, and 96-day cured samples made with both de-ionized water and saturated NaCl solution as the mixing water. Permeability measurements using both the medium pressure cell for gas permeability and the water permeability cell have continued. SEM microstructural observations were made on samples 19-J and 20-J which were cured for 36 and 63 days. Other characterizations included compressive strength measurements, x-ray diffraction studies, and IR absorption spectra.

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 cements 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 period July 1 to September 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 at

temperatures up to at least 315°C or higher and set with good compressive and bond strengths. Physical tests have continued and long-term aging has begun.

A short-term test program is being added to determine the effects of thermal cycling on one of the SwRI 150°C hydrothermal cements.

University of Rhode Island

T.J. Rockett, 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 report period data on the solubility of glass in 30% phosphoric acid at 40°C and 90°C were obtained. The data show that a critical concentration of silica exists above which the glasses do not interact with phosphate solutions and therefore could not form geothermal cements. Below the critical composition interaction is rapid and could result in a cement reaction.

Experiments to determine the stability of reactive phases in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ are in progress. Future plans for equilibrium studies and for glass corrosion studies have been outlined.

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 have been 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 two hydrothermal cements, a PC, API Class G and API Class H.

The test program consists of the determination of compressive strength, shear bond strength, and permeability after exposure to water at 195°C . The effect of thermal cycling on bond strength will also be determined. Results to date are summarized in Appendix 6.

Task 4. Placement Technology

Thickening time tests are being performed on cements identified at Colorado School of Mines, Dowell, Battelle's Columbus Laboratories, Southwest Research Institute and BNL. Test results are given in Appendices 1-4.

Task 7. Administrative

During the current report period, three "Monthly Administrative Letters" were submitted to DGE and Quarterly Progress Report No. 9³ was issued. A paper entitled "The Influence of the Curing Agent Concentration

and Curing Temperature on the Thermostability of Styrene-Acrylonitrile-Acrylamide-Trimethylolpropane Trimethacrylate Copolymer Systems" has been accepted for publication in the "Journal of Applied Polymer Science". Another paper entitled "The Effect of Dicalcium Silicate and Tricalcium Silicate on the Thermal Stability of Vinyl-Type Polymer Concrete" has been accepted for publication in "Cement and Concrete Research".

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APPENDIX 1

DEVELOPMENT OF GEOTHERMAL WELL COMPLETION SYSTEMS

PHASE II: Progress Report No. 3
July - September, 1978

Contributors:

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EXECUTIVE SUMMARY

Phase II of Dowell's DOE contract has continued this quarter with work to develop a new and improved geothermal cementing system as well as continued effort to build a data base of information on systems already in use. The initial screening program has already identified several promising systems that will undergo more rigorous testing.

All of the thickening time tests have been completed for the systems entered into the initial screening program. Of those passing that test a high percentage have successfully met the minimum short term compressive strength requirements. Over the long term, however, many of these systems are expected to fail. Permeability evaluation has also been completed. Next quarter, the crucial bonding and expansion tests will be initiated.

Research to evaluate the effect of heavy (Salton Sea) brines on silica stabilized Portland cement systems continued this quarter. It has been determined that the particle size of the silica is an extremely important factor in a cement's ability to withstand degradation when exposed to geothermal conditions. Silica within the particle size range of 3 to 10 μm is optimum for stabilization due to rate of solubility considerations. Also, as a general rule, coarser grind cements are easier to stabilize than fine grinds.

Dynamic brine exposure testing of cement systems deemed to have promise has begun at the East Mesa Test Facility near San Diego, California. Testing at the Nilands, California, test site is scheduled to start soon. Also, the laboratory geothermal simulator, D-BETA, is nearing completion and will be operational in mid-November. The dynamic tests are very rigorous and should serve as a very good indicator of a cement's suitability for use in a geothermal environment.

The chemical studies phase of the project will begin running at full pace next quarter with the new advanced x-ray diffraction instrumentation coming on line in November. Meanwhile, some significant discoveries have been made. Research concerning the carbonaceous calcium silicate phase, scawtite, has established that it is a binder of inferior strength when compared with xonotlite, a closely related compound. However, scawtite appears to enhance strength when present in minor quantity. An anomalous x-ray diffraction peak of high intensity at $3.50\text{\AA}$ is often seen on patterns of Class G cements that contain silica-rich extenders. The presence of the phase, as yet unknown, that is giving rise to the $3.50\text{\AA}$ peak seems to have a significant effect on binder strength. Work will continue next quarter to identify this potentially important "mystery phase".

Only limited work has been done this quarter on the furfuryl alcohol/powdered coal cement system due to the problematic exotherms associated with the polymerization reactions. Before further work can be performed, the violent nature of this system must be controlled. Toward that end, automated calorimetry studies are currently in progress.

INTRODUCTION

Phase II of Dowell's contract research on behalf of the Department of Energy is continuing on schedule. This report documents work performed during the months July through September, 1978. Significant progress has been made in the four principal areas of study: (1) placement studies, (2) stability measurements, (3) chemical studies, and (4) development of non-Portland systems.

As was the case with the previous progress report, COO/4190-3, much of this report consists of an extensive amount of data presented in tabular form. For the sake of brevity, only data obtained during July, August, and September is included here.

SCREENING PROGRAM

The initial series of screening tests is continuing in accordance with the procedure outlined in progress report COO/4190-1. Data generated during this quarter is presented in Tables 1, 2, and 3. To obtain an understanding of the new data's significance, the reader is encouraged to compare the new results with those listed in previous progress reports.

All systems have been evaluated in terms of thickening time as of this quarter. Additional thickening time tests will, of course, be performed when new systems are proposed or if more complete data is required. Table 1 lists the thickening time results obtained this quarter.

A high percentage of cement systems have met the minimum compressive strength requirements of 500 psi within one day and 1000 psi within seven days. It is expected, however, that some of the systems will fail the 28 day high temperature test program and be dropped from the testing schedule. Strength data for this quarter is listed in Table 2. A gradual strength

development with time is the traditional preferred behavior of well cement systems; however, some very promising systems have been observed to lose some strength initially and then steadily gain to a high compressive strength. According to early data, the lime-silica systems generally develop only marginal strength when cured at 227°C. An exception to this observation is the system containing Needles fly ash. Compressive strength testing will continue in the next quarter.

Permeability testing has been completed for the initial series of cement systems. In Table 3, this quarter's permeability results are listed. The systems that underwent permeability evaluation were those consisting of Ciment Fondu (high alumina cement), Class J with sodium silicate, lime-silica, lime-silica with aluminum hydroxide, lime-silica with perlite and bentonite, and lime-silica with magnesia.

Next quarter, the bonding and expansion tests are scheduled to begin. The data obtained from these tests will be very informative as to the proposed systems' ability to perform satisfactorily in a geothermal environment.

STABILITY MEASUREMENTS

Cement systems that appear to be potentially suitable for use in geothermal wells are currently being tested for stability when exposed to corrosive brines at high temperatures. Testing is being performed under both static and dynamic conditions in brines that were considered to be representative of those encountered under actual conditions. Static testing has been in progress for a long time; however, dynamic testing has begun only recently.

Static Brine Testing

Tests to evaluate the effect of heavy (Salton Sea) brines on silica stabilized Portland cement systems were continued this quarter. Last quarter it was noted that some systems were not performing as expected when exposed to the heavy brine. Certain cements were not converting to xonotlite when heated to temperatures of 232 to 325°C; as a result, these cements were much weaker and more porous than expected. Additional tests have confirmed that Portland cement stabilized with 40% fine silica sand (70-200 mesh or 100 μ m) will deteriorate when contacted by a hot dense brine while Portland cement stabilized with 35 to 40% silica flour (average 10 μ m) is not seriously affected. The Portland cement stabilized with 100 μ m silica is reasonably stable in fresh water or 3% brine (sea water). It moderately deteriorates at 325°C when exposed to brines containing 15% salts, and seriously deteriorates when in contact with brines containing 25% salts.

Deterioration was also noted in weak brines if the mix water used to prepare the slurry contained 10% or more sodium chloride. Addition of a greater amount of 100 μ m silica improves the stability somewhat, but even doubling the addition of 100 μ m silica to 80% by weight of cement is not as effective as the use of 10 μ m silica flour.

These studies have indicated that Portland cement slurries are stabilized by addition of silica in a rather narrow particle size range. Particle sizes finer than 325 mesh (44 μ m) were able to stabilize the Portland cement against deterioration in hot brine solutions. Addition of extremely fine silica, 3 μ m or less, will result in very thick slurries associated with air entrainment. Such cement is much lighter in weight when set, and higher porosity and permeability with lower strength is observed. As a general rule, coarse ground cements such as Class H or coarse Class A are more

easily stabilized than fine cements such as Class G or Universal Atlas slag cement.

Of course, temperature plays a critical role in determining silica's ability to stabilize Portland cement. Deterioration of Portland cement with 100µm silica began to occur from 150 to 232°C when exposed to heavy brines. At 150°C there was essentially no difference between the stabilizing ability of fine silica sand and silica flour. At 232°C and 325°C, however, there was a great deal of difference in that the silica sand cement was much poorer. With many cement formulations there was little difference between the 232 and 325°C counterparts.

Based on data obtained here, it is apparent that in most cases up-hole exposure should not be as severe as bottomhole brine exposure. The elevated temperature up-hole will tend to dry out the formation and exposed cement. Testing has indicated that exposure to dry heat does not deteriorate cement as severely as does brine. X-ray diffraction analysis of cements exposed to dry heat shows a marked loss of crystallinity and suggests that hydration and phase transition reactions cease.

As was reported last quarter, x-ray analysis of the cements has continued to indicate that the strongest samples are predominantly xonotlite (C_6S_6H). The weaker and more porous cements, characterized by addition of 100µm silica sand, are mainly composed of kilchoanite (C_3S_2H). The difference in binder composition is believed to be mainly due to a lower rate of solubility of silica in brine solutions. Use of finer silica exposes much more surface area and reduces the brine's effect on solubility. The saturation point of silica in brine is irrelevant because the excess calcium hydroxide

produced by Portland cement immediately reacts with solubilized silica; in so doing, a saturation level is prevented. Likewise, the stability of xonotlite in brine is not a factor because all samples were subjected to identical conditions.

A complete listing of static brine exposure data for the third quarter is provided by four tables: 4, 5, 6, and 7. Table 4 lists the composition of all the systems tested with both light and heavy brines. Compressive strength data for heavy brine exposures is listed in Table 5, while Table 6 lists permeability results for these systems. Compressive strength and permeability of cements exposed to light and medium density brines is reported in Table 7.

Dynamic Brine Testing

Dynamic testing is now in progress. This phase of testing was delayed primarily because of limits of practicality. Since only a limited number of samples can be tested dynamically, it was thought that only the most promising systems should be allowed to undergo this evaluation. The dynamic testing program is divided into three major efforts: field testing at two sites in California, East Mesa and Nilands, and laboratory simulation in Tulsa.

The laboratory geothermal simulator D-BETA (Dynamic Brine Exposure Testing Apparatus) is nearing the completion stage and is scheduled to begin operating in mid-November. The D-BETA is a recirculating system in which a synthetic brine of composition similar to that found at East Mesa (see previous report) flows past up to 32 one inch diameter cylindrical cores. The rate of flow is controllable and the brine may be heated to 350°C with pressures up to 3100 psi. After exposure to the brine for specified periods of time the cement cores will be removed and examined. To prevent corrosion of vital

components of the system, most of the D-BETA has been fabricated out of Inconel 600 alloy. A schematic diagram of the D-BETA is found in Figure 1. Figure 2 is a draftsman's rendering of how the instrument will appear when completed.

Field testing of cement samples under actual flowing brine at the East Mesa Test Facility near San Diego has been initiated. The testing apparatus is very similar to the D-BETA in basic design. The field apparatus differs in that it is possible to isolate each cell from the brine circulation allowing for convenient sample removal. Also, the 300°F brine does not recirculate but instead simply makes one pass through the cells and is flashed to the atmosphere. As can be seen in Figure 3, a photograph of the apparatus, the brine flows from the well into a 25 gallon surge tank. Then, the brine passes through the sample cells which, like the D-BETA, are made of Inconel 600 alloy steel. Next, the brine is simply released to the atmosphere.

The samples currently in the test apparatus will remain there for only one month in an effort to evaluate the feasibility of the present design. Thirty-two different cement formulations, the compositions of which are listed in Table 8, are involved in this initial "shake-down" effort. If no difficulties are encountered in the initial program, the extended program will begin with cement samples undergoing continuous exposure for up to two years. The extended tests will probably evaluate only 16 cement formulations because a sample of each system must be removed after periods of 3 and 6 months, and 1 and 2 years to monitor progress. As a result, two of the four test chambers, each of which hold eight samples will not be disturbed for two years. The other two test chambers will be replenished with fresh samples when the 3 and 6 month specimens are removed.

Testing at the Nilands facility has yet to be initiated due to preoccupation with the East Mesa program. Once the East Mesa tests are running smoothly, the Nilands program will begin to receive attention.

CHEMICAL STUDIES

Other than routine x-ray analysis of cement samples from other aspects of this project, the chemical studies program to elucidate the reactions and kinetics of cement hydration and strength retrogression has progressed rather slowly this quarter. This state of affairs is primarily due to the fact that much of the planned research is contingent upon the use of the sophisticated computerized x-ray diffraction system that was ordered during the first quarter. The system has been delivered and will be operational by mid-November; thus, at long last, this important phase of the project will progress unhindered from now on.

Work continued this quarter to determine whether the phase scawtite ($\bar{C}_7S_6CH_3$), which is commonly encountered when cement is cured at elevated temperatures in the presence of carbonates, is a suitable substitute for xonotlite (C_6S_6H) as a binder in geothermal wells. Compressive strength measurements have indicated that scawtite is generally of lower strength than xonotlite when it is the predominant phase; however, there is evidence to suggest that scawtite enhances strength when present in minor amounts. Before actual data is reported, however, the cement samples will be analyzed by the new x-ray system. The new system is capable of performing excellent semi-quantitative analysis of phases in cement due to greatly increased signal to noise ratio and a significant reduction of interference from preferential orientation.

Careful scrutiny of the x-ray diffraction patterns of a number of cements cured under geothermal conditions has resulted in the

discovery of an anomaly that may have significant bearing on the strength of the binder. When Class G cement is mixed with a silica rich extender such as perlite, bentonite, or volcanic ash, an unusually intense peak at $3.50\text{\AA}$ often appears on the x-ray pattern.

A particularly striking illustration of this may be seen with a recent system, H22. H22 was a slurry consisting of Class G cement with 35% silica flour, 2% bentonite, 8.5% perlite, and 0.3% lignin/sugar retarder. The mix water was saturated with salt. The slurry was cured at 150°C under saturated steam pressure for 1 day. Two separate specimens were cured from the same slurry: one in glass (H22G) and the other in brass (H22B). Then the cement samples were cured in a 26% NaCl-CaCl_2 heavy brine at 325°C for 7 days in a steel tube. Figure 4 is the XRD pattern for the glass-cured cement and Figure 5 is the pattern for the brass-cured counterpart. Xonotlite is the principal binder in both specimens with some halite present due to the nature of the mix water and brine. The intensities of the xonotlite and halite peaks appear to be absolutely identical in both patterns; the $3.50\text{\AA}$ peaks, however, are not. The H22B pattern shows a $3.50\text{\AA}$ intensity much lower than that of the H22G pattern. The compressive strength of H22B is 2530 psi while H22G is only 690 psi.

This relationship between $3.50\text{\AA}$ peak intensity and compressive strength has been exhibited by several other samples. There is no apparent correlation between compressive strength and the nature of the curing container because some samples cured in glass have been stronger than their brass-cured counterparts.

The $3.50\text{\AA}$ problem has been brought to the attention of Dr. H. F. W. Taylor at the University of Aberdeen, Scotland. Dr. Taylor is an internationally recognized authority on calcium silicate chemistry and mineralogy. Samples of these

cements were sent to his laboratory for analysis with his specialized instrumentation. Dr. Taylor confirmed the presence of the anomalous intensity of the 3.50Å peak, and determined that preferential orientation is not responsible. The xonotlite 002 peak is located at 3.50Å; if preferential orientation was occurring, the xonotlite 001 peak at 7.05Å would also be enhanced. Thus, the exaggerated intensity at 3.50Å must be due to a separate phase. Dowell and Dr. Taylor's laboratory have run extensive tests on the samples but nothing definite has been determined as yet.

Though little more than a hunch, a form of silica, or a calcium silicate of very low Ca/Si ratio structurally related to keatite seems to be the most likely possibility at the present time. Keatite is tetragonal and has its strongest powder lines at 3.42Å (100), 3.72Å (70) and 4.50Å (20) (JCPDS card 13-26). JCPDS card 21-503, for the closely related β -spodumene, gives what looks to be a better pattern.

When these cements are leached with boiling water, the 3.50Å intensity drops dramatically. At first a soluble salt was suspected but no powder data to support this has been found. Phases such as β -spodumene are known to be readily altered on drying or exposure to unusual temperature and humidity conditions; thus, the beginnings of an explanation may be surfacing. All of this is a long shot but further work is planned to define more exactly the range of starting materials and curing conditions from which the 3.50Å peak can be obtained. Curing of the silica rich extenders in the presence of a small amount of calcium hydroxide under hydrothermal conditions is planned to try to synthesize a phase similar to β -spodumene. Also, more detailed SEM studies of these cements including electron microscopy and selected area diffraction will be performed. Because this "mystery phase" appears to have a rather dramatic impact on strength, it is important that its identity be discovered.

NON-PORTLAND SYSTEMS

Work with the furfuryl alcohol and powdered coal system has not been pursued to a significant extent this quarter. The violent exotherms associated with this system must be controlled before further study can be initiated. Currently, the system is being evaluated by automated calorimetry to better define the nature of the reactions that are responsible for the troublesome exotherms. It is anticipated that further study will be instituted next quarter.

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ADDITIVE CODES

<u>Code</u>	<u>Material</u>
ALOH	Aluminum hydroxide, $\text{Al}(\text{OH})_3$
BENT	Bentonite
COAL	Powdered coal
DE	Diatomaceous earth
FA/L	La Due fly ash
FA/N	Needles fly ash
ILLM	Ilmenite, FeTiO_3
PERL	Expanded perlite
PP	Plaster of paris, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$
R1	Retarder - proprietary blend of sugar and lignin derivatives
R2	Retarder - proprietary blend of lignin and inorganic salts
SF	Silica flour - $\leq 10 \mu\text{m}$ avg.
SAND	Medium fine silica - $\leq 100 \mu\text{m}$ avg.
SR	Sugar retarder
SSS	Sodium metasilicate, solid

TABLE I Thickening Time of Systems Tested During Third Quarter, 1978

Cement	Additives Present (% BWOC)					Retarder		Thickening Time (hr:min)
	Code	%	Code	%	%H ₂ O	Code	%	
Class J	ALOH	5	-	-	44	R1	0.1	1:47
Class J	ALOH	5	-	-	44	R1	0.4	+5:00
Slag	SF	35	-	-	56	R1	1.5	+6:00
Slag	SF	35	FA/N	79	93	R1	1.25	+5:00
Slag	SF	35	SSS	2.5	122	R1	1.25	+6:00
Slag	SF	35	SSS	1.5	122	R1	0.75	+5:00
1:1 Lime-Silica	-	-	-	-	96	R1	0.3	1:28
1:1 Lime-Silica	ALOH	7	-	-	96	R1	1.0	3:44
0.4:1 Lime Silica	-	-	-	-	100	R1	1.0	+6:00
0.42:1 Lime-Silica	-	-	-	-	142	R1	0.5	0:58
Ideal "B"	SAND	35	-	-	56	R1	1.0	1:42
Ideal "B"	SAND	35	-	-	56	R1	1.2	3:19
Ideal "B"	SAND	35	-	-	56	R3	0.4	0:42
Ideal "B"	SF	35	-	-	56	R1	1.5	+6:00
Ideal "B"	SF	35	NaCl	21	56	R1	1.0	+5:00

TABLE 2 Compressive Strength Results For Third Quarter, 1978

Cement	Code	%	Additives (% BWOC)						% Water	Comp. Str. (psi)					
			Code	%	Code	%	Code	%		227°C		316°C			
										1 Day	3 Day	1 Day			
G	(1) Sand	35	R1	1.0	-	-	-	-	54	3388	2300*	4862			
	(2) SF	35	R1	1.0	-	-	-	-	54	3581	5000	5150			
	(3) SF	35	R1	1.0	FA/N	79	-	-	52	2521	5350	3619			
	(4) SF	35	R1	1.0	Perl	8.5	Bent	2	116	1612	891*	1054			
	(5) SF	35	R1	0.8	NaCl	20	-	-	54	4125	4713	3687			
	(6) SF	35	R1	1.0	NaCl	5.4	-	-	54	5187	5350	6781			
	(7) SF	35	R1	1.0	KCl	20	-	-	54	3362	5032	3706			
	(8) SF	35	R1	1.0	KCl	5.4	-	-	54	5025	5987	4984			
	(9) SF	35	R1	1.0	DE	8.86	-	-	91.2	--	2866	--			
	(10) SF	35	R1	1.0	Coal	27	-	-	63	--	2548	--			
	(11) SF	35	R1	1.0	ILLM	27	-	-	63	--	3057	--			
										227°C		316°C			
										3 Day	7 Day	1 Day	3 Day	7 Day	
B	(1) Sand	35	R1	1.2	-	-	-	-	56	3064	3412	6350	4437	5312	
	(2) SF	35	R1	1.5	-	-	-	-	56	5350	(5856)	--	--	(2731)	
	(3) SF	35	R1	0.6	Perl	8.5	Bent	2	118	497	(1526)	--	--	(884)	
	(4) SF	35	R1	1.0	KCl	22	-	-	60	2070	3012	3250	3431	3750	
	(5) SF	35	R1	1.0	NaCl	22	-	-	60	3439	3637	2968	3406	3187	
	(6) SF	35	R1	1.0	FA/N	79	-	-	54	3407	4787	4606	4062	--	
SLAG	(1) SF	35	R1	1.25	-	-	-	-	56	1529	3775	4344	3450	3975	
	(2) SF	35	R1	1.25	FA/N	79	-	-	93	4904*	1200	4587	3575	4600	
	(3) SF	35	R1	1.25	SSS	1.5	-	-	122	--	--	1066	1108	450	
	(4) SF	35	R1	1.25	PP	10	NaCl	7.4	74	1592	2887	2625	1969	1187	
Fondu	(1) R1	1.5	R2	1.5	-	-	-	-	50	987	--	--	--	--	
	(2) FA	85	R1	1.5	R2	1.5	-	-	81	--	1372	--	--	1090	
Silica-Lime ¹															
	(1) R1	0.7	--	--	-	-	-	-	96	605	1175	--	--	656	
	(2) ALOH	7	R1	1.0	-	-	-	-	96	796	900	--	--	725	
	(3) Perl	8.5	Bent	2.0	R1	0.7	-	-	110	287	325	--	--	400	
	(4) FA/N	79	R1	1.0	-	-	-	-	130	2771	1975	--	--	1752	
	(5) R1	0.3	--	--	-	-	-	-	96	414	599	--	--	450	
	(6) R1	0.7	--	--	-	-	-	-	100	1388	1617	--	--	165	
	(7) R1	0.7	--	--	-	-	-	-	142	1452	995	--	--	187	
										227°C		316°C			
										1 Day	3 Day	7 Day	1 Day	3 Day	7 Day
J	(1) R1	0.4	--	--	-	-	-	-	43.5	4406	5385	4300	4106	--	4543
	(2) FA/N	79	R1	0.4	-	-	-	-	75	240	968	928	2837	--	3700
	(3) Perl	8.5	Bent	2.0	R1	0.4	-	-	106	57	--	467	516	--	828
	(4) Bent	4.0	R1	0.4	-	-	-	-	65	2102	2439	2015	731	--	901
	(5) Bent	8.0	R1	0.4	-	-	-	-	86	795	2102	2275	856	--	907
	(6) NaCl	17	R1	0.2	-	-	-	-	44	3899	3630	2237	3431	--	2692
	(7) KCl	4.4	R1	0.2	-	-	-	-	44	4125	4140	5187	3712	--	4062
	(8) SSS	2.0	R1	0.2	-	-	-	-	90	426	382	925	700	--	1125

TABLE 3: Fluid Permeability Measurements For Third Quarter, 1978

Cement samples cured for 3 days at 227°C

<u>System</u>	<u>Permeability(md)</u>	<u>System</u>	<u>Permeability(md)</u>
G1	0.016	Fondu 1	0.101
G2	< 0.001		
G3	< 0.001	J1	< 0.001
G4	0.05	J2	0.03
G5	0.04	J4	< 0.001
G6	0.01	J5	< 0.001
G7	0.03	J6	< 0.001
G8	0.015	J7	< 0.001
G9	0.058	J8	0.3
G10	-		
G11	< 0.001	L1	0.304
G12	0.069	L2	0.106
		L3	0.54
B1	0.035	L4	< 0.001
B2	< 0.001	L5	0.105
B3	0.07	L6	0.01
B4	0.005	L7	< 0.001
B5	0.07		
B6	< 0.001		
Slag 1	< 0.001		
Slag 2	< 0.001		
Slag 4	0.01		

TABLE 4: Systems Used in Evaluating Static Brine Exposure or Salt Cement Systems. Additive Codes at End of This Table.

No.	Cement	Additives % By Weight of Cement						% Water
		%R1	Code	Amt	Code	Amt	Code	
Z1	Permanente "G"	0.4	S180	40	--	-	--	54
Z2	"	0.4	S120	40	--	-	--	54
Z3	"	0.4	S60	40	--	-	--	54
Z4	"	0.4	S30	40	--	-	--	54
Z5	"	0.4	S10	40	--	-	--	54
Z6	"	0.4	S3	40	--	-	--	54
Z7	"	0.4	SAND	40	--	-	--	54
Z8	Permanente "G"	0.4	SF	40	--	-	--	54
Z9	Tijeras "B"	0.5	S180	40	--	-	--	54
Z10	Tijeras "B"	0.5	S120	40	--	-	--	54
Z11	Tijeras "B"	0.5	S60	40	--	-	--	54
Z12	Tijeras "B"	0.5	S30	40	--	-	--	54
Z13	Lonestar H	0.4	S180	40	--	-	--	50
Z14	Lonestar H	0.4	S120	40	--	-	--	50
Z15	Lonestar H	0.4	S60	40	--	-	--	50
Z16	Lonestar H	0.4	S30	40	--	-	--	50
Z17	Permanente "G"	0.3	S180	40	Perl	8.5	Bent	2 102
Z18	Permanente "G"	0.3	S120	40	Perl	8.5	Bent	2 102
Z19	Permanente "G"	0.3	S60	40	Perl	8.5	Bent	2 102
Z20	Permanente "G"	0.3	S30	40	Perl	8.5	Bent	2 102
Z21	Permanente "G"	0.3	S10	40	Perl	8.5	Bent	2 102
Z22	Permanente "G"	0.3	S3	40	Perl	8.5	Bent	2 102
Z23	Permanente "G"	0.3	SAND	60	Perl	8.5	Bent	2 108
Z24	Permanente "G"	0.3	SAND	80	Perl	8.5	Bent	2 114
Z25	Oklahoma "A"	0.3	SAND	40	Perl	8.5	Bent	2 102
Z26	(coarse grind)	0.3	SAND	60	Perl	8.5	Bent	2 108
Z27	Tijeras "B"	0.3	SAND	40	Perl	8.5	Bent	2 102
Z28	Tijeras "B"	0.3	SAND	60	Perl	8.5	Bent	2 108
Z29	Lonestar "H"	0.3	SAND	40	Perl	8.5	Bent	2 102
Z30	Lonestar "H"	0.3	SAND	60	Perl	8.5	Bent	2 108
Z31	Slag IS	0.3	SAND	40	Perl	8.5	Bent	2 102
Z32	(Univ. Atlas)	0.3	SAND	60	Perl	8.5	Bent	2 108
Z33	Permanente "G"	0.4	SAND	40	NaCl	20	--	54
Z34	"	0.4	SAND	60	NaCl	22	--	60
Z35	"	0.4	SF	35	NaCl	20	--	54
Z36	Tijeras "B"	0.5	SAND	40	NaCl	20	--	54
Z37	"	0.5	SAND	60	NaCl	22	--	60
Z38	"	0.5	SF	35	NaCl	20	--	54
Z39	Lonestar "H"	0.4	SAND	40	NaCl	20	--	50
Z40	"	0.4	SF	35	NaCl	20	--	50

TABLE 4 (cont'd)

Z41	Permanente "G"	0.5	SAND	40	Perl	8.5	NaCl	10	102
Z42	"	0.5	SAND	40	Perl	8.5	NaCl	18	102
Z43	"	0.5	SAND	40	Perl	8.5	NaCl	37	102
Z44	"	0.5	SAND	60	Perl	8.5	NaCl	39	108
Z45	"	0.5	SAND	40	Perl	8.5	NaCl	0	102
Z46	"	0.5	SF	35	Perl	8.5	NaCl	37	102
Z47	"	0.5	SAND	40	Perl	8.5	KCl	37	102
Z48	Permanente "G"	0.4	SAND	40	SSS	2	KCl		125
Z49	"	0.4	SAND	40	Bent	12	NaCl	2	118
Z50	"	0.4	SAND	60	Bent	12	NaCl	2	123
Z51	"	0.4	SAND	20	DE	20	NaCl		125
Z52	"	0.5	SAND	40	SSS	2	NaCl		125
Z53	"	0.5	SAND	40	Bent	12	NaCl	2	118
Z54	"	0.5	SAND	60	Bent	12	NaCl	2	123
Z55	"	0.5	SAND	20	DE	20	NaCl		125

Additive Code -	Code	Material
	Bent	Bentonite
	DE	Diatomaceous earth
	KCl	Potassium chloride
	NaCl	Sodium chloride
	Perl	Expanded perlite
	Rl	Proprietary retarder blend - sugar and lignin derivatives
	SSS	Sodium metasilicate, solid
	SAND	70-200 mesh sand average 100 micron
	SF	Silica, average 10 micron
	S-180	70-100 mesh silica, average 180 micron
	S-120	100-170 mesh silica, average 120 micron
	S-60	170-325 mesh silica, average 60 micron
	S-30	Ground silica sedimentation sep. avg. 30 micron
	S-10	Ground silica sedimentation sep. avg. 10 micron
	S-3	Ground silica sedimentation sep. avg. 3 micron

TABLE 5: Compressive Strengths of Systems Evaluated in Static Heavy Salton Sea Brine at Various Temperatures - Systems descriptions given in Table 4. Heavy brine (approximately 25%) composition given in COO/4190-3, Phase II progress report No. 2, Table 3. Compressive strengths are expressed in lb/sq. in.

System	1 Day Cure Fresh Water	150°C		232°C		325°C		Dry Heat 325°C
	150°C	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	28 Day
Z1	3400			700	700	1000	675	5900
Z2	2650			925	1050	1625	850	5050
Z3	2925			1625	1525	1325	1225	4700
Z4	3625			6350	5725	4225	4325	3850
Z5	5200			6800	4800	4525	4750	6125
Z6	5725			4850	4525	3150	2800	5900
Z7	2725			1450	675	1250	400	3150
Z8	5400			3050	3975	6125	4525	6025
Z9	4000			1125	925	1675	1025	2725
Z10	4350			1150	1450	2900	2400	3500
Z11	5125			2175	2550	3575	3550	5150
Z12	7400			8125	7300	6050	5548	9450
Z13	1750			1725	1300	1650	1925	1575
Z14	2175			2575	3375	3400	3075	1800
Z15	3725			5450	7100	6350	5650	3150
Z16	5357			9725	6050	5175	4625	8200
Z17	1350	1625	1425	800	1450	400	500	1425
Z18	1325	2650	1450	2375	3350	675	600	1700
Z19	1300	2975	2350	3700	3475	3225	2975	2500
Z20	3132	3025	2825	3750	2950	2800	4225	3775
Z21	3656	2750	2525	3625	3125	2925	3450	4600
Z22	2000	2675	2300	1950	1650	1650	2475	--
Z23	1350	2325	2000	2900	2100	1025	1300	1875
Z24	1325	2375	2575	3075	2975	2950	3025	1950
Z25	893					2950	2875	1075
Z26	1368					2775	3250	2175
Z27	1013					1525	1275	1400
Z28	1840					2800	3400	2700
Z29	1045					2900	3475	1500
Z30	1618					2025	3000	1825
Z31	925					425	975	1300
Z32	1125					1275	1500	1675
Z33	5625	--	7500	--	775	1500	1350	7625
Z34	5475	--	5950	--	800	1575	1025	6750
Z35	5350	--	6525	--	4225	4650	4700	--
Z36	5275	--				775	750	--
Z37	5050					875	600	5475
Z38	5325					4725	4350	5750
Z39	1100					750	675	3650
Z40	3200					4700	5800	--
Z41	2050			200	375	25	75	2775
Z42	1950			175	225	200	150	1200
Z43	350	--	2200	125	200	150	125	350
Z44	750			275	300	325	150	475
Z45	900			775	450	800	725	1875
Z46	1025	--	1950	1450	1625	1525	2375	900
Z47	1600			100	125	50	75	1000
Z48	650					25	5	1600
Z49	875					25	300	2025
Z50	925					1550	1400	1225
Z51	525					175	650	725
Z52	525					50	50	575
Z53	1000					25	150	950
Z54	850					1200	1475	1775
Z55	500					200	475	1600

TABLE 6: Permeabilities in Millidarcies of Systems Evaluated in Static Heavy Salton Sea Brine at Various Temperatures. Systems descriptions given in Table 4. Heavy brine (approximately 25%) composition given in COO/4190-3. Phase II progress report No. 2, Table 3.

System	1 Day Care	150°C				232°C				325°C				Dry Heat	
	Fresh Water	150°C				232°C				325°C				28 Day	325°C
	150°C	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	Air	Water		
Z1	0.045			1.77	4.75	3.80	3.71	0.41	0.051						
Z2	0.044			0.92	0.42	2.49	3.17	0.64	0.032						
Z3	0.049			0.49	0.22	2.24	1.13	0.52	0.030						
Z4	0.003			0.008	0.012	0.066	0.035	0.20	0.016						
Z5	< 0.001			0.002	0.002	0.007	0.010	0.11	0.002						
Z6	0.002			0.004	0.002	0.016	0.023	--	---						
Z7	0.043			1.55	5.43	2.77	4.47	0.71	---						
Z8	< 0.001			0.001	0.011	0.017	0.012	0.021	0.001						
Z9	0.053			1.69	1.15	1.52	3.17	0.66	0.034						
Z10	0.047			1.83	0.43	0.88	2.38	0.36	0.005						
Z11	0.004			0.30	0.072	0.75	0.30	0.22	0.015						
Z12	0.003			0.009	0.009	0.066	0.045	0.009	---						
Z13	0.080			2.17	2.83	1.73	4.00	33.0	15.1						
Z14	0.052			0.091	0.061	0.21	0.40	18.6	2.67						
Z15	0.006			0.009	0.017	0.041	0.061	0.26	0.031						
Z16	0.001			0.004	0.006	0.014	0.041	0.008	0.001						
Z17	0.094	0.017	0.021	1.01	1.38	16.9	19.0	4.9	2.1						
Z18	0.056	0.007	0.014	0.26	0.36	6.5	7.6	3.3	0.20						
Z19	0.033	0.001	0.014	0.072	0.094	0.34	0.26	0.54	0.025						
Z20	0.005	< 0.001	0.001	0.031	0.052	0.040	0.043	0.11	0.005						
Z21	0.001	< 0.001	0.001	0.032	0.022	0.050	0.024	0.22	0.040						
Z22	0.019	< 0.001	< 0.001	0.035	0.031	0.058	0.063	--	---						
Z23	0.043	0.002	0.015	0.123	0.24	0.51	1.17	0.69	0.052						
Z24	0.047	0.002	0.006	0.066	0.095	0.25	0.23	1.4	0.024						
Z25	0.005					0.29	0.35	1.5	0.063						
Z26	0.004					0.078	0.034	0.56	0.043						
Z27	< 0.001					1.02	0.85	0.82	0.10						
Z28	< 0.001					0.11	0.102	0.24	0.19						
Z29	< 0.001					0.22	0.011	0.44	0.030						
Z30	< 0.001					0.049	0.043	0.48	0.17						
Z31	< 0.001					1.2	0.16	1.9	0.63						
Z32	< 0.001					0.45	0.098	0.47	0.16						
Z33	0.004	--	< 0.001	--	2.3	3.30	2.06	0.12	0.018						
Z34	< 0.001	--	< 0.001	--	3.7	2.62	2.58	0.15	0.007						
Z35	< 0.001	--	< 0.001	--	0.041	0.023	0.001	--	---						
Z36	0.001					4.47	3.71	--	---						
Z37	< 0.001					2.72	2.45	0.061	0.005						
Z38	< 0.001					0.072	0.058	0.18	0.007						
Z39	0.030					8.45	5.24	0.92	0.026						
Z40	< 0.001					0.022	0.040	0.14	---						
Z41	0.004			2.2	2.7	15.2	15.2	0.51	0.057						
Z42	0.006			2.6	6.3	23.8	>10	0.64	0.34						
Z43	0.004	--	0.001	15.2	10.1	--	10	4.0	0.63						
Z44	0.008			6.8	7.3	25.4	14.0	2.9	0.32						
Z45	0.001			1.31	2.45	19.0	>10	2.2	0.49						
Z46	0.004	--	0.001	0.043	0.20	0.11	0.059	1.4	0.10						
Z47	0.010			20.0	10.8	--	--	0.82	0.66						
Z48	0.15					--	--	5.92	--						
Z49	0.008					--	--	0.66	0.021						
Z50	0.004					4.35	5.07	1.10	0.041						
Z51	0.069					--	--	2.51	0.45						
Z52	0.113					--	--	5.02	--						
Z53	0.010					--	--	1.07	0.12						
Z54	0.004					4.75	3.90	0.30	0.025						
Z55	0.025					4.91	--	0.31	0.022						

TABLE 7: Effect of Light and Medium Density Brine on Slurries Containing Salt. For data on strengths in heavy brine, see Table 5. For data on permeability in heavy brine see Table 6. Compressive strengths are expressed in lb/sq. in. and permeability in millidarcies.

System	325°C Compressive Strength(psi)				325°C Permeability(md)			
	3% Brine		15% Brine		3% Brine		15% Brine	
	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day
Z41	925	825	50	75	4.75	4.0	15.2	16.0
Z42	225	550	200	150	11.9	8.6	16.5	--
Z43	600	875	150	100	5.3	9.9	--	--
Z44	1150	1175	250	1325	3.4	2.4	18.1	14.0
Z45	1950	1725	1075	1375	3.9	2.2	15.8	1.3
Z46	2325	1700	1375	1900	0.04	0.12	0.068	0.059
Z47	125	125	50	50	16.5	--	--	--

TABLE 8:

Initial Dynamic Field Exposure Systems East Mesa Test Facility, California

		Additives (% BWOC Unless Otherwise Indicated)								
	Cement	Additive	%	Additive	%	Additive	%	Additive	%	%H ₂ O
1.	Kaiser G	SAND	35	SR	1	--	-	-	-	54
2.	Kaiser G	SF	35	SR	1	-	-	-	-	54
3.	Kaiser G	SF	35	SR	1	FA/N	79	-	-	52*
4.	Kaiser G	SF	35	SR	1	PERL	8.5	BENT	2	116
5.	Kaiser G	SF	35	SR	0.8	NaCl	37	-	-	54
6.	Kaiser G	SF	35	SR	1	NaCl	10	-	-	54
7.	Kaiser G	SF	35	SR	1	KCl	10	-	-	54
8.	Kaiser G	SF	35	SR	1	DE	8.86	-	-	91.2
9.	Kaiser G	SF	35	SR	1	COAL	27	-	-	62.9
10.	Unadeep J	SR	0.4	--	-	--	-	-	-	43.5
11.	Unadeep J	SR	0.4	FA/N	79	-	-	-	-	42*
12.	Unadeep J	SR	0.4	PERL	8.5	BENT	2	-	-	106
13.	Unadeep J	SR	0.4	BENT	4	-	-	-	-	65
14.	Unadeep J	SR	0.4	BENT	8	-	-	-	-	86
15.	Unadeep J	SR	0.2	NaCl	37	-	-	-	-	44
16.	Unadeep J	SR	0.2	KCl	10	-	-	-	-	44
17.	Unadeep J	SR	0.2	SSS	2	-	-	-	-	90
18.	(1:1)									
	Lime-Silica	SR	0.7	--	-	-	-	-	-	96
19.	(1:1)									
	Lime-Silica	SR	1	Al ₂ O ₃	7	-	-	-	-	96
20.	(1:1)									
	Lime-Silica	SR	0.7	PERL	8.5	BENT	2	-	-	110
21.	(1:1)									
	Lime-Silica	SR	1	FA/N	79	-	-	-	-	130
22.	(0.4:1)									
	Lime:FA/N	SR	0.7	-	-	-	-	-	-	100
23.	(0.4:1)									
	Lime:POZZ	SR	0.7	-	-	-	-	-	-	142
24.	Ideal B	SAND	35	-	-	-	-	-	-	56
25.	Ideal B	SF	35	SR	1.5	-	-	-	-	56
26.	Ideal B	SF	35	SR	0.6	PERL	8.5	BENT	2.0	118
27.	Ideal B	SF	35	SR	1.0	KCl	37	-	-	60
28.	Ideal B	SF	35	SR	1.0	NaCl	37	-	-	60
29.	Ideal B	SF	35	SR	1.0	FA/L	79	-	-	54
30.	Kaiser G	SAND	35	SR	1.0*	FA/N	79	-	-	52
31.	Kaiser G	SAND	35	SR	1.0	PERL	8.5	BENT	4	116
32.	Ideal B	SAND	35	SR	0.6	PERL	8.5	BENT	4	118

* By weight of ash + cement

Figure 1. Schematic diagram of dynamic brine exposure testing apparatus (D-Beta).

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

Figure 3. Photograph of dynamic brine testing apparatus at East Mesa, California.

Figure 4. X-ray diffraction pattern for sample H22G.

Figure 5. X-ray diffraction pattern for sample H22B.

APPENDIX 2

Quarterly Technical Progress Report
June-August, 1978

on

HIGH TEMPERATURE CEMENTING MATERIALS
FOR COMPLETION OF GEOTHERMAL WELLS

to

BROOKHAVEN NATIONAL LABORATORY

September 30, 1978

by

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Under Contract No. 420825-S

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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

HIGH TEMPERATURE CEMENTING MATERIALS FOR COMPLETION OF GEOTHERMAL WELLS

Quarterly Technical Progress Report

June-August 1978

INTRODUCTION AND SUMMARY

Compressive strength and cement-to-metal casing bond strength evaluations of cementing compositions cured for 1 day, 7 days, and 28 days at 450F and saturated steam pressure were continued. Also thickening time measurements on several compositions with 30% Class J oil well cement were made. The experiments were carried out both at room temperature and in the hot can assembly. The strength measurements were carried out under these two different conditions to emphasize the importance of high temperatures and steam pressures (which the cementing compositions are subjected to at the geothermal well site) on the mechanical properties of the cements. As the data presented indicate, the 24-hour compressive strengths of all the cementing compositions studied (either measured at room temperature or in the hot can) exceed the required minimum value of 1000 psi. Very little or no deterioration of strength is observed upon longer time exposures to high temperatures and steam pressures as indicated by the strength values of samples cured for 7 and 28 days.

Reduction of cement content from 40 to 30% also did not noticeably affect the strength values, indicating that the additives used develop certain cementing qualities under the curing conditions. Increase in the thickening times, however, was noticed with compositions containing 30% Class J oil well cement compared to those with 40% Class J cement. Cement-to-metal bond strengths continue to be very high regardless of the test conditions (room temperature or hot can assembly) indicating that casing-to-cement interface would not present a problem to efficiency or the life of the geothermal well.

No permeability measurements were made during the last quarter. Modifications of the permeability apparatus is necessary for obtaining more accurate values than previously reported. Actual permeabilities of these cementing compositions are believed to be much lower than the values reported in the last Quarterly Technical Progress Report. problems were encountered in sealing the permeability samples in the pressure cell.

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 and presented in previous reports.

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

During the last quarter, the laboratory research efforts concentrated on the following tasks of Phase III studies:

Task No. 1 - Thickening time measurements

Task No. 2 - Compressive strength measurements

Task No. 4 - Cement-to-metal bond strength measurements.

Thickening time measurements were made of five cementing compositions with 30% Class J oil well cement.

Compressive strength measurements were made of compositions containing 30 and 40% Class J oil well cement, and various additives. These measurements were conducted on samples after 1 day, 7 days, and 28 days of curing at 450F and saturated steam pressure.

Cement-to-metal bond strength was also made of the same compositions both at room temperature and in the hot can assembly (at 300F and saturated steam pressure).

Task No. 1 - Thickening Time Measurements

Thickening times are determined using the API thickening time tester as described in the previous report. Figures 1 through 10 summarize the thickening time data plotted as viscosity vs. D.C. voltage, viscosity vs. time and temperature vs. time.

Viscosity vs. D.C. voltage plots present the calibration data from which the viscosities are determined as a function of voltage (temperature) at any given time during the course of thickening time experiment. Because the lowest experimental point giving the quantitative relationship between the viscosity and voltage is at a viscosity value of about 10 Uc, the relationship between voltage and viscosity in the 0 to 10 Uc voltage range is obtained by extrapolating the calibration curve through the origin. This procedure is of a questionable accuracy, as illustrated in Figure 5. In view of the fact, however, that the cement slurries do not lose their pumpability up to about 100 Uc, the above extrapolation does not take anything away from the practical value of the technique. Although the viscosity values up to the first measured voltage (e.g. 4.7 volts) are not very accurately known, they are well below the critical value of 100 Uc. Therefore, this method of extrapolation serves its practical purpose.

The question addressed in the thickening time experiments is not as much what the precise value of viscosity is during the cementing operation (as long as it is well below 100 Uc) but how long does it take, under the specified thermal and pressure conditions, for the viscosity of the slurry to reach 100 Uc, a value beyond which the pumping of the cement slurry becomes impractically difficult. Figures 1, 3, 5, 7, and 9 show the calibration curves obtained prior to thickening time measurements of samples. The calibration of the instrument is done with use of paratone calibration oil, the viscosity-temperature relationship of which is known over a range of 5 to 100 Uc.

Figure 2, 4, 6, 8, and 10 depict the viscosity and temperature profiles for the different cementing compositions. The temperature profiles indicate the heating rate of the slurries during the experiment. A very significant feature of the viscosity vs time curves is that viscosities remain relatively constant with time as a function of temperature rise as opposed to gradually increasing. This is a very desirable feature of the slurries. An ideal cement slurry in geothermal well completion operations should exhibit low (≈ 50 Uc) and constant viscosity all throughout the cementing operation and set shortly after the cementing of the well is completed. The observed viscosity behavior of the cementing compositions indicate that these composition exhibit this property, that is, low and constant value over a long time and a sudden rise in the viscosity. In Figure 8, for example, the cement slurry retains its original viscosity up to about 90 minutes, then rises to about 65 Uc (which is still quite pumpable) and remains at that value up to 350 minutes before rising to a value above 100 Uc. Constant viscosity is also desirable in preventing possible problems in pumping operations that may result due to variations in viscosities. The pumping rates would be influenced by variable slurry viscosities and this may cause practical problems such as uneven pumping rates and even more serious problems of equipment breakdown.

The measured thickening time values of the cement slurries studied continue to be lower than anticipated-based on the static experiments conducted in small pressure containers. Empirical thickening time values obtained from the static experiments indicate that the lowest thickening time values should be 150 to 200 minutes as opposed to 75-90 minutes obtained with the API thickening time tester.

A careful examination of the thickening time data (Figures 2,4,6,8, and 10) reveals that the thickening times are adversely affected by blast furnace slag contents, that is, increased amounts of blast furnace slags result in shorter thickening times. Silica flour and pozzolan, however, lengthen the thickening times.

Task No. 2 - Compressive Strength of Cements

Compressive strength measurements on compositions of 30 and 40% Class J oil well cement were continued. Measurements were conducted both at room temperature and using the hot can assembly described in the previous report.

Tables 1, 2, and 3 present the compressive strength data on the cementing compositions containing 30 % Class J oil well cement after 1 day, 7 days, and 28 days curing at 450 F and saturated steam pressure. Carboxy methyl cellulose was used as an admixture with one exception (carboxy methyl hydroxy ethyl cellulose was used in composition with 30% Class J cement, 40% pozzolan and 30% blast furnace slag). Water-to-solids ratio was 0.5 in all the samples cured. The 24-hour compressive strength values in all cases are greater than 1000 psi. No significant deterioration in the compressive strengths of cements is observed with longer exposure times.

Tables 4 and 5 summarize the compressive strength of cements with 40% Class J oil well cement after 1 day and 7 days curing at 450 F and saturated steam pressure. These measurements were only made at room temperature and atmospheric pressure.

As Tables 2 and 3 indicate, the effects of longer time exposures to high temperatures and pressures on the compressive strengths depend on the cementing compositions. All the cementing compositions show increase in the compressive strengths from 1 day to 7 days exposure. Compositions with pozzolan and blast furnace slags, however, continue to exhibit increased strength beyond 7 days exposure. Also cementing compositions with two additives, in general, show higher strengths than samples with one additive. In any case, all the cementing compositions tested exhibit adequate or higher strengths even when tested under the simulated geothermal conditions.

The differences in the compressive strength values measured under two different conditions (room temperature and hot can assembly) can be attributed

(i) partly to the difference in the quality of the test specimens and (ii) largely to differences in the high temperature stability (chemical and mechanical) of the various cementing compositions.

Task No. 3 - Permeability of Cements

A number of permeabilities were reported in the previous report with values 0.1 md or lower, indicating that cementing materials under investigation meet the permeability criterion. Also, the point was made that the reported permeability values were believed to be considerably higher than true permeabilities of the samples. These high values are largely due to the difficulties of effectively sealing the space between the sample and the walls of the permeability cell. The gasket materials can not withstand pressures up to 200 psi without some leakage. Necessary modifications in the measurement techniques and sample size are being made to alleviate the sealing problem in question.

Task No. 4 - Cement-to-Metal Bond Strength

Cement-to-metal bond strength measurements were carried out both at room temperature and in hot-can assembly using 1-inch diameter specimens cast around 1/4-inch steel rods, as previously described. The cement-to-metal bond strength is described as the force required to push the metal rod through the cast cements with unit area of interface between the metal and cement.

Tables 6 and 7 summarize the cement-to-metal bond strength values for various cementing compositions. It is obvious from the reported data in Table 6 that bond strengths measured in the hot-can assembly are even higher than the room temperature values. The thermal expansion difference between the metal and cement is probably the major reason for the observed higher bond strength values.

FUTURE WORK

Presently, copper-coppersulfate (Cu-CuSO_4) half-cell assembly is being set up for the studies of corrosive effects of cement on the well casing. The experiments are anticipated to start sometime in October.

Thickening time measurements will be continued on remaining compositions of interest with 30% Class J cement. Also some analytical characterization of cementing compositions (with XRD, SEM) will be made.

TABLE 1. COMPRESSIVE STRENGTH OF COMPOSITIONS WITH 30% CLASS J
OIL WELL CEMENT CURED AT 450 F FOR 1 DAY

Cement Composition	Amounts	Admixture	W/S	Compressive Strength, room temp.	Compressive Strength, hot can
SF P	40 30	CMC	0.5	3050	2600
SF BFS	30 40	"	"	1720	1650
P BFS	30 40	"	"	3550	1450
P BFS	40 30	CMHEC	"	2750	1800
SF BFS B	35 30 5	"	"	1470	1300
BFS	70	"	"	2050	1900
P	70	"	"	2180	1200
BFS SF	60 10	"	"	2050	2100
P SF	60 10	"	"	2050	1600

TABLE 2. COMPRESSIVE STRENGTH OF COMPOSITIONS WITH 30% CLASS J
OIL WELL CEMENT CURED AT 450 F FOR 7 DAYS

Cement Composition	Amounts	Admixture	W/S	Compressive Strength, room temp.	Compressive Strength, hot can
SF P	40 30	CMC	0.5	3500	2610
SF BFS	30 40	"	"	3600	2850
P BFS	30 40	"	"	3800	2200
P BFS	40 30	CMHEC	"	2600	2200
SF BFS B	35 30 5	"	"	2500	1400
BFS	70	"	"	1800	1300
P	70	"	"	2300	2200
BFS SF	60 10	"	"	2850	1400
P SF	60 10	"	"	3200	2500

TABLE 3. COMPRESSIVE STRENGTH OF COMPOSITIONS WITH 30% CLASS J
OIL WELL CEMENT CURED AT 450 F FOR 28 DAYS

Cement Composition	Amounts	Admixture	W/S	Compressive Strength, room temp.	Compressive Strength, hot can
SF	40	CMC	0.5	1911	1400
P	30				
SF	30	"	"	3567	1300
BFS	40				
P	30	"	"	3758	3100
BFS	40				
P	40	CMHEC	"	2293	1900
BFS	30				
SF	35	"	"	1580	1150
BFS	30				
B	5				
BFS	70	"	"	1274	1050
P	70	"	"	1605	1500
BFS	60	"	"	2420	1800
SF	10				
P	60	"	"	1834	1400
SF	10				

TABLE 4. COMPRESSIVE STRENGTHS OF COMPOSITIONS WITH 40% CLASS J
OIL WELL CEMENT AT 450 F FOR 1 DAY

Cement Composition	Amounts	Admixture	W/S	Compressive Strength, room temp.	Compressive Strength, hot can
SF BFS	30 30	CMC	0.6	1912	
L SF	30 30	"	0.7	1174	
SF P	30 30	"	0.55	1918	
P BFS	30 30	"	0.65	3341	
SF P BFS	20 20 20	"	0.6	2777	
SF BFS	30 30	BA	1.0	1860	
L SF	30 30	"	"	1626	
SF P	40 30	CMC	0.5	2276	2480
SF P	30 30	BA	0.55	75.40	
P BFS	30 30	"	0.6		
SF L P	20 20 20	"	0.65	1429	
SF	20	"	0.55	2447	

TABLE 5. COMPRESSIVE STRENGTHS OF COMPOSITIONS WITH 40% CLASS J
OIL WELL CEMENT AT 450 F FOR 7 DAYS

Cement Composition	Amounts	Admixture	W/S	Compressive Strength, room temp.	Compressive Strength, hot can
SF	30	CMC	0.5	2558	
BFS	30				
L	30	"	"	1588	
SF	30				
SF	30	"	"	1687	
P	30				
P	30	"	"	3307	
BFS	30				
SF	20	"	"	3188	
P	20				
BFS	20				
SF	30	BA	"	1165	
BFS	30				
L	30	"	"	2263	
SF	30				
SF	30	"	"	1541	
P	30				
P	30	"	"	3104	
BFS	30				
SF	20	"	"	1138	
L	20				
P	20				
SF	20	"	"	2002	
L	20				
BFS	20				
SF	20	"	"	3142	
P	20				
BFS	20				

TABLE 5. (Continued)

Cement Composition	Amounts	Admixture	W/S	Compressive Strength, room temp.	Compressive Strength, hot can
SF	60	CMC	0.5		
SF	20	"	"	1923	
BFS	40				
SF	30	"	"	1472	
BFS	30				
SF	40	"	"	1800	
BFS	20				
SF	30	"	0.55		
P	30				
SF	60	BA	0.5	983	
SF	20	"	0.6	1580	
BFS	40				
SF	30	"	"	1443	
BFS	30				
SF	40	"	0.65	1232	
BFS	20				
SF	30	"	0.6	1400	
P	30				

TABLE 6. CEMENT-TO-METAL BOND STRENGTH OF COMPOSITIONS
WITH 30% CLASS J OIL WELL CEMENT CURED AT
450 F FOR 1 DAY

Cement Composition	Amounts	Admixture	W/S	Compressive Strength, room temp.	Compressive Strength, hot can
SF	40	CMC	0.5	510	675
P	30				
SF	30	"	"	407	478
BFS	40				
P	30	"	"	338	510
BFS	40				
P	40	CMHEC	"	662	280
BFS	30				
SF	35	CMC	"	293	350
BFS	30				
B	5				
BFS	70	"	"	210	535
P	70	"	"	232	363
BFS	60	"	"	446	694
SF	10				
P	60	"	"	484	535
SF	10				

TABLE 7. CEMENT-TO-METAL BOND STRENGTH OF COMPOSITIONS
WITH 30% CLASS J OIL WELL CEMENT CURED AT
450 F FOR 1 DAY

Cement Composition	Amounts	Admixture	W/S	Compressive Strength, room temp.	Compressive Strength, hot can
SF	40	CMC	0.5	662	
BFS	20				
SF	40	"	"	550	
P	30				
SF	30	"	"	200	
BFS	40				
P	30	"	"	240	
BFS	40				
P	40	CMHEC	"	485	
BFS	30				
SF	35	CMC	"	166	
BFS	30				
B	5				
BFS	70	"	"	160	
P	70	"	"	204	
BFS	60	"	"	200	
SF	10				
P	60	"	"	250	
SF	10

Figure 1. Consistency calibration curve.

Figure 2. Temperature and viscosity profiles from the API high temperature consistometer.

Figure 3. Consistency calibration curve.

Figure 4. Temperature and viscosity profiles from the API high temperature consistometer.

Figure 5. Consistency calibration curve.

Figure 6. Temperature and viscosity profiles from the API high temperature viscometer.

Figure 7. Consistency calibration curve.

Figure 8. Temperature and viscosity profiles from the API high temperature consistometer.

Figure 9. Consistency calibration curve.

Figure 10. Temperature and viscosity profiles from the API high temperature viscometer.

APPENDIX 3

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
June 1 - August 31, 1978

September 1, 1978

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

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Introduction

The objectives of this research are to develop new high temperature cementing materials for geothermal wells. The work involves investigation of compositions which lie dominantly within the systems $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$.

During this past quarter approximately 30 runs have been completed and other long term runs are in progress to establish equilibrium phase relations and to determine the properties of modified class J and calcium-aluminate cements reacted at high temperatures and pressures. X-ray diffraction/phase equilibria studies within the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ have concentrated on delineating phase relations near the join: xonotlite-chrysotile. Differences in the viscosities of slurries were related to systematic differences in total composition (e.g. cement + Al_2O_3 , MgO, or retarding additives) and different forms of added SiO_2 (tripoli, minusil, quartz sizes). Microhardness as an indicator of strength was measured on 36, 63, and 96-day cured samples made with both de-ionized water and saturated NaCl solution as the mixing water. Permeability measurements using both the medium pressure cell for gas permeability and the water permeability cell have continued. SEM microstructural observations were made on samples 19-J and 20-J which were cured for 36 and 63 days. Other characterizations included compressive strength measurements, x-ray diffraction studies, and IR absorption spectra.

Phase Equilibria/X-ray Diffraction Studies

During the past quarter, the experimental phase equilibria effort has centered around the join: xonotlite-chrysotile shown projected on the system CaO-MgO-SiO_2 in Fig. 1. Preliminary experiments had shown that mixtures lying along this join exhibited superior strength properties. Starting materials were CaO , MgO , and SiO_2 (both 5μ Minusil and tripoli). Compositions of mixtures investigated are given in Table 1. Starting

TABLE 1
Compositions of Mixtures

Mixture Number	Weight Percent			
	Class J Cement	MgO	CaO	SiO_2
5	90	10	-	--
8	44	10	-	46
18	85	15	-	--
19	70	20	-	10
20	86	10	4	--

materials were mixed with either deionized water or a saturated NaCl solution. Table 2 summarizes the experimental procedure for each of 22 runs made in the above system.

All experiments were carried out in crimped noble metal tubes except for 5-J-400-10-0.45 and 18-J-400-96-0.36 which were hydrothermally cured in water-filled autoclaves. Generally speaking, crystallinity increased as the amount of MgO in the mixtures increased. Reaction products for the 63-day deionized water runs consisted of three phases. In mixture 20 evidence of chrysotile is very minor. This mixture consists of xonotlite and diopside. Mixture 18 consists of a trace of chrysotile and major amounts of xonotlite and diopside. Mixture 19 continues this three-phase pattern showing increased chrysotile, major xonotlite, and increased diopside.

Infrared spectra and the scanning electron microscope were also used as tools to identify the stable phases in the class J cement sample

Figure 1. Location of starting materials relative to the "join" xonotlite-chrysotile. Hydrates are underlined.

19-J hydrothermally cured for 36 and 63 days. Previous workers (Taylor, personal communication) had shown that scawtite $[\text{Ca}_7\text{Si}_6\text{O}_{18}(\text{CO}_3) \cdot 2\text{H}_2\text{O}]$ was a stable phase when Class J cement samples were hydrothermally cured. As can be seen in Fig. 2 sample 19-J contains very little CO_3^{2-} thus eliminating the possibility that scawtite was a major component of the stable phases. Also, the phases present do not contain a large percentage of OH^- or H_2O . The scanning electron microscope was used to determine both the micro-structure: needles, plates, and prisms (see Fig. 3), and to determine the approximate

TABLE 2

Hydrothermal Runs Using Class J Cement Pastes with Either
Deionized Water or Saturated NaCl as Mixing Water

Sample #	Temperature °C	Pressure (psi)	Curing Time (days)	Mixing Water		Hydrothermal Curing
				DI	H ₂ O NaCl	
4A-J-400-44-0.1*	400	10,000	44	X		crimped tubes
4B-J-4-0-44-0.2	400	10,000	44	X		crimped tubes
4C-J-400-44-0.3	400	10,000	44	X		crimped tubes
4D-J-400-44-0.00	400	10,000	44	dry		crimped tubes
5 -J-400-10-0.45	400	10,000	10	X		autoclave
18 -J-400-36-0.45	400	10,000	36	X		crimped tubes
19 -J-400-36-0.45	400	10,000	36	X		crimped tubes
19T-J-400-36-0.45**	400	10,000	36	X		crimped tubes
20 -J-400-36-0.45	400	10,000	36	X		crimped tubes
18 -J-400-63-0.45	400	10,000	63	X		crimped tubes
19 -J-400-63-0.45	400	10,000	63	X		crimped tubes
19T-J-400-63-0.80**	400	10,000	63	X		crimped tubes
20 -J-400-63-0.45	400	10,000	63	X		crimped tubes
5N-J-400-63-0.40***	400	10,000	63		X	crimped tubes
18N-J-400-63-0.45	400	10,000	63		X	crimped tubes
19N-J-400-63-0.45	400	10,000	63		X	crimped tubes
20N-J-400-63-0.40	400	10,000	63		X	crimped tubes
5N-J-300-63-0.40	300	10,000	63		X	crimped tubes
18N-J-300-63-0.45	300	10,000	63		X	crimped tubes
19N-J-300-63-0.45	300	10,000	63		X	crimped tubes
20N-J-300-63-0.40	300	10,000	63		X	crimped tubes
18 -J-400-96-0.36	400	10,000	96	X		autoclave

*4A-J-400-44-0.1: Mixture 4, experiment A, cement type J, 400°C, 44 days hydration, 0.1 w/s ratio.

**T = tripoli - all other runs made with added 5 μ Minusil as silica source.

***N denotes that saturated NaCl solution was used to prepare cement paste.

composition of each of the structure types. All three forms showed the apparent presence of calcium, magnesium, and silicon by energy-dispersive x-ray analysis (possibly with thin fibers, elements from adjacent crystals would be detected as well as the elements contained). Diposide (CaMgSi₂O₆)

Figure 2. Infrared spectra of sample 19-J-400-63-0.45.

Figure 3. SEM photographs of samples #19 and #20 cured for 36 and 63 days at 400°C and 10,000 psi.

with a short prismatic habit has been positively identified (by x-ray diffraction) as one of the major constituents of sample 19-J (both the 36 and 63-day cured). This is consistent with the composition determined on the prisms, which is thus unambiguous. In addition the main features of the spectra of pure diposide (Rutstein and White, 1971) are apparent in the IR spectrum of Fig. 2. Some of the bands from the current sample are multiple and the extra shoulders must result from the additional phases which are present [in fact the shoulder at $\sim 1200\text{ cm}^{-1}$ and major peak at $\sim 970\text{ cm}^{-1}$ are characteristic of xonotlite (Roy and Johnson, 1967), while chrysotile has diagnostic peaks at ~ 470 and $\sim 630\text{ cm}^{-1}$ in addition to peaks in the higher wave number Si-O vibration region].

Work is continuing around this join in an effort to establish the validity and extent of the stability triangle as well as to delineate the effects of NaCl on the reaction products at both 400 and 300°C.

Property Measurements

Microhardness

Microhardness measurements have been made on five sets of four compositions each of Class J cement mixed with 10, 15, and 20 percent MgO. The four compositions (5, 18, 19, 20) shown in Fig. 1 had been hydrothermally cured as shown in Table 2.

Figure 4 shows that the microhardness, as an indicator of strength, increased between the 36 and 63-day cured samples and then decreased for the 96-day sample. Part of this difference may reflect a slightly different procedure in sample preparation. The 96-day samples were hydrothermally treated as 1-inch diameter by 2-inch long cylinders whereas the 36 and 63-day cured samples were hydrothermally cured in 5 mm diameter by 2 cm noble metal crimped tubes. Even so there is a systematic increase in the microhardness as the amount of MgO within the sample increased. At present samples containing 20 percent MgO with Class J cement are being hydrothermally cured at 400°C and 10,000 psi for 96 days. These data should be available for the next quarterly report.

Two sets of samples with identical compositions as above had been prepared with a saturated NaCl solution and hydrothermally treated at 300 and 400°C for 63 days. In all samples microhardness measurements indicated a lower strength in the NaCl-containing samples. This is very different from room temperature cured samples for which NaCl gave higher strength than those made with deionized water. The phase determinations by x-ray diffraction have not yet been made on the NaCl containing sample, but may help explain the difference.

Class J cement samples made with lower w/s ratios (0.1, 0.2, 0.3 water/solid ratios and a dry sample) were hydrothermally cured at 400°C and 10,000 psi and 44 days. As expected, these were found to have the highest strengths. A microhardness of 44 kg/mm² was found for the dry class J cement sample. In all future sample preparations the water/solid ratio will be kept to the minimum feasible and if possible be kept below 0.50.

The microhardness for composition 8 shown in Fig. 1 after hydrothermal curing (400°C and 10,000 psi) was 8.5 kg/mm²; after an additional 137 days curing at room temperature in a desiccator the microhardness was 10.2 kg/mm².

MICROHARDNESS MEASUREMENTS FOR:
 CLASS J CEMENT PASTE SAMPLES
 HYDROTHERMALLY CURED AT 300 & 400 °C
 10,000 psi (68.9 MPa) FOR 36, 63, 8 96 DAYS.

Figure 4. Microhardness for modified Class J cement samples.

TABLE 3
Gas and Water Permeability Measurements on Calcium-Aluminate and
Class J Cement Samples

Sample #	Gas Pressure (psi)	Gas Permeability (darcys)	Water Permeability @ 2000 psi (darcys)
HYD- 9-CA-380-5-0.50	6 16	1.64×10^{-2} 2.48×10^{-2}	not possible
HYD-10-CA-380-5-0.50	9 18	1.95×10^{-2} 2.65	not possible
HYD-11-CA-380-5-0.50	14 26	6.45×10^{-2} 8.29	not possible
18A-J-400-96-0.36	infin.	3.95×10^{-5} w epoxy seal	6.93×10^{-5} w/o epoxy seal
18B-J-400-96-0.36	-	-	2.63×10^{-5} w epoxy seal (350 ml water)
*18C-J-400-96-0.36	infin.	8.90×10^{-6} w epoxy seal	-
*18D-J-400-96-0.36	-	-	8.92×10^{-5} w epoxy seal (165 ml water)

*Curing includes room temperature curing for 50 additional days.

Compressive Strength

Compressive strength had been measured on a cylindrical, modified Class J cement neat paste (Class J cement: 85%; MgO: 15%) sample which had cured at 400°C, 10,000 psi for 96 days. The strength of the 1-inch diameter by 2-inch long sample was 168 kg/cm². Microhardness for this sample cured for 96 days was approximately 21.1 kg/mm².

Permeability

Both gas and water permeability were measured on modified calcium aluminate (Type CA) and Class J cement samples which were hydrothermally cured. The calcium-aluminate cement paste samples HYD-9, 10, 11 (65, 55, and 45% SiO₂) with 5 percent perlite were very porous. (They also had relatively high w/s ratios, = 0.5). [HYD-9, 10, and 11 have the same compositions as HYD-6, 7, 8 given in the June 1978 quarterly report.] It was not possible

Figure 5. Gas permeability using the medium pressure cell.

to measure gas permeabilities in excess of 26 psi, therefore an extrapolated water permeability at finite pressure was also not possible. See Table 3. Samples with similar composition as above with with another type of Ca-aluminate cement (type "CB") are presently curing at 400°C and 3000 psi (20.7 MPa).

As seen in Table 3 and Figs. 5 and 6, the gas and water permeabilities of four different pieces of identically-treated modified Class J cement samples agree within an order of magnitude (9×10^{-6} to 9×10^{-5} darcys).

Figure 6. Gas and water permeability measurements of sample 18-J.

Permeability measurements were made on samples which were hydrothermally cured in stainless steel rings, then measured immediately (#18A and #18B). Another set, #18C and #18D, were cured hydrothermally for 96 days then cured for an additional 50 days at room temperature. Comparing water permeability on samples 18B and 18D shows a slightly lower permeability immediately after hydrothermal treatment only by a factor of 4. The gas permeability comparison is reversed and is different by a factor of 2.

Viscosity

Viscosity measurements were made using the Rheolog viscometer model 5X HBT on modified calcium-aluminate and Class J cements with various admixtures. Differences in the viscosities of slurries were related to systematic differences in total composition (e.g. cement + Al_2O_3 , MgO, or retarding additives) and different forms of the added SiO_2 (tripoli, minusil, quartz sizes). Of the admixtures used a lignosulfonate-type retarder was found to be the most effective in reducing viscosity of the Ca-aluminate-based cements, while the superplasticizer admixtures were not as effective. See Figure 7a. The identification of the interrelationships between retarding additive and two different Ca-aluminate cements ("R" and "S") have shown that there is a significant difference in the behavior of the two cements using a lignosulfonate retarder. See Fig. 8. As expected, an increasing quantity of lignosulfonate decreased the viscosity of the mixture in all comparable situations. Our studies are continuing on both these cements.

For comparison a Class J cement was modified by the addition of Al_2O_3 and MgO in 10 and 20 percent quantities. An increase of from 10 to 20 percent Al_2O_3 reduced the viscosity whereas an increase of 10 to 20 percent MgO increased the viscosity by a factor of 5 as shown in Fig. 7d. The viscosity of a MgO slurry (300 g MgO with w/s = 1.5) was very high just after mixing, then decreased with time. The maximum speed at which the modified paddle would turn initially was 10 rpm. After time, as indicated by the direction of the arrows in Fig. 9, the viscosity decreased and the shear stress of the slurry corresponded to approximately 2.5 millivolts after approximately 12 minutes mixing.

Figure 7. Viscosity measurements on calcium-aluminate (a,b) and Class J cement pastes (c,d) with various admixtures.

Figure 8. Comparison between two calcium aluminate cement paste viscosities with Lignosulfonate added as a retarder.

Figure 9. Viscosity of MgO with a w/s ratio of 1.5.

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Personnel

The research for this period has been under the direction of Dr. Della M. Roy with assistance from Dr. Elizabeth L. White. A graduate student, C. Langton, and research technicians D. Wolfe-Confer and G. Zimmerman have been involved in the research to various extents. Effective September 1st, Dr. Michael Grutzeck has joined the project as a senior project associate and N. Hermanowicz will be replacing D. Wolfe-Confer as a research technician.

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

TECHNICAL PROGRESS REPORT NO. 4

July - September 1978

SwRI Project No. 02-5083

BNL Contract No. 427964-S

to

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

October 15, 1978

APPROVED:

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ABSTRACT

A research program to develop improved cements for use in geothermal well completions was begun in October 1977 at Southwest Research Institute. This fourth quarterly technical progress report includes work accomplished during the period July - September 1978. Selection has been made of several formulations for use at 315°C and above. Physical testing of the various formulations has included compressive and bond strengths and permeability to water.

I. INTRODUCTION

In October 1977, Southwest Research Institute (SwRI) 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 fourth quarter of Brookhaven National Laboratory Contract No. 427964-S at SwRI.

During the period of July 1 to September 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 at temperatures up to at least 315°C or higher and set with good compressive and bond strengths. Physical tests have continued and long-term aging has begun.

A short-term test program is being added to determine the effects of thermal cycling on one of the SwRI 150°C hydrothermal cements.

II. REVIEW AND EVALUATION

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

III. SwRI HIGH-TEMPERATURE CEMENT RESEARCH

A. Formulation Optimization

1. General

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 metal salts, for instance, prepared with each different silicate will exhibit varied reactivities. The stoichiometries of the various formulations are empirically determined on the basis of final product properties.

2. Recipes

We have extended our optimization procedures to find the "optimum formulation" for use over 316°C (600°F). In Table I, Recipe #4 appears to be the best for use over 316°C (600°F). It was pumpable for over 3 hrs at this temperature. After 48 hrs at 260°C (500°F), Recipes #2 and #3 were in the gel state. The basic formulations of the SwRI hydrothermal cement systems for use at temperatures above 200°C are listed in Table I.

B. Physical Properties Evaluation

1. Placement Ability

We have continued to modify our various high-temperature formulations to respond better to curing variables. Mixes of the regular hydrothermal cement formulation containing aluminum oxide (Al_2O_3) have been run for 5 hrs at 232°C before thickening. Additions of zirconia have shown promise for use above 250°C.

TABLE I

SwRI Hydrothermal Cement Formulations

<u>Ingredients</u>	<u>#1 at 204°C</u>	<u>#2 at 260°C</u>	<u>#3 at 260°C</u>	<u>#4 at 316°C</u>
Sand	50	50	50	-
Flour	25	25	25	50
Britesil	10	10	10	10
Anhydrous Sodium Silicate	10	10	10	10
Bentonite	-	-	-	5
Al(OH) ₃	7	-	-	-
Al ₂ O ₃	-	5	-	-
ZnO	-	-	-	-
ZrO	-	-	7	-
LaO ₂	-	-	-	7
H ₂ O	18	18	18	23

The high-temperature formulations were also modified by the additions of the following: vanadium pentoxide, titanium dioxide, ferric oxide, or aluminum phosphate. Thus far we have had fair results at curing temperatures of 260-316°C with the addition of titanium oxide. However, consistometric runs above 230°C have not given sufficient thickening times. At 205°C we have been able to obtain 3 hrs or more pumping time using zirconia as the activating agent. Above 230°C we have not had 30 minutes.

We have also modified the high-temperature formulation by the addition of several lanthanum compounds. These included lanthanum carbonate, lanthanum hydrate, and lanthanum oxide. Consistometric tests have shown that these compounds would be pumpable for at least 2 hrs at 260°C (500°F). Further thickening tests were run using small quantities of lanthanum oxide in the regular hydrothermal formula, and at 330°C, the cement remained pumpable for 2 hrs. Another test at 340°C was pumpable for 1 hr.

2. Compressive Strength

One-inch cylinders and two-inch cubes have been made from the various formulations, cured for periods up to 14 days, and tested for compressive strength. Results of 7-day aging in a saturated steam and brine environment (at 260°C/2500 psi) are as shown.

<u>Specimen No.</u>	<u>Compressive Strength (psi)</u>
Z1 (ZrO ₂)	6920
Z2	6975
Z3	5800
Z4	6350
A1 [Al(OH) ₃]	2300
A2	2410
A3	2810
A4	2460

Three sets of specimens which had been aging for 14 to 28 days at temperatures of 288°C and 316°C and at a pressure of 2500 psi were all scrapped because of autoclave malfunctions. These tests are being duplicated.

A set of specimens was made using zirconium oxide and another was made using lanthanum hydrate. These specimens were removed from the high-temperature chamber after being aged for 14 days in medium-pressure saturated steam and brine. Strength tests have not been made as yet.

3. Bond Strength

Shear bond strength tests have been made on specimens cured in steel cylinders. These are 3-in. I.D., with a 1-in. steel pin centered by use of a machined base plate. The slurry was poured into these molds and cured at 260°C/2500 psi in a saturated steam and brine environment.

<u>Specimen No.</u>	<u>Bond Strength (psi)</u>
Z1 (ZrO ₂)	1150
Z2	1170
Z3	1025
Z4	1100
A1 [Al(OH) ₃]	480
A2	475
A3	520
A4	495

4. Other Research

During the reporting period, SwRI has submitted a proposal to perform certain tests on our 150°C hydrothermal cement formulations for possible application in the remedial cementing of the EE-1 hot-dry-rock geothermal well at Los Alamos, New Mexico.

The test program proposed will consist primarily of the cyclical test matrix. Each cycle will be 48 hrs long, cooling down from 200°C to 35°C, followed by reheating to 200°C. A complete test will be on the basis of 1, 3, and 7 cycles, of 48 hrs each cycle, requiring a total of about 35 days including bond tests. Tests will be run at a pressure of about 6200 psi, equivalent to the HDR bottom-hole pressure of 5000 psi at a 9600-ft depth, plus a pumping pressure of 1200 psi. The actual placement temperature is expected to be from 150 to 180°C; however, BHT will ultimately reach 200°C. At the end of each sequence of cycles, samples will be removed from the autoclave for the purpose of making bond strength tests, and then replaced for the next sequence of thermal cycling.

Test specimens will be of two types, with duplicates of each:

- (1) Pipe-in-pipe, or steel rod-in-pipe, with cement in the annulus between pipes. This is our standard bond test.
- (2) Pipe-in-rock. This would closely simulate the conditions down-hole with the three different thermal coefficients to deal with. We believe that 8-in. long sections will be sufficient for obtaining good bond strength data.

Compressive strength and permeability tests will also be made on the cement after exposure to the cyclical conditions. These specimens will be removed concurrently with the 1-, 3-, and 7-cycle sequences of the above bond tests.

It is our intention to show that our hydrothermal cement will form an excellent bond to the casing, with bond strengths of at least 1000

psi. If the casing shrinks away from the SwRI cement, breaking the bond, then expands again with an increase in heat flux, the cement bond will "heal" and nearly regain its maximum strength within 24 to 48 hrs.

Approval for the additional work has been given. Test work will commence as soon as arrangements for funding have been completed.

APPENDIX 5

BNL Contract 418691-S
PHOSPHATE BONDED GLASS CEMENTS
FOR GEOTHERMAL WELLS

Quarterly Technical Report No. 5
July to September, 1978

from

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

to

Process Technology Division
Department of Applied Science
Brookhaven National Laboratories
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ABSTRACT

Data on the solubility of glass in 30% phosphoric acid at 40°C and 90°C are presented. The data show that a critical concentration of silica exists above which the glasses do not interact with phosphate solutions and therefore could not form geothermal cements. Below the critical composition interaction is rapid and could result in a cement reaction.

The experiments to determine the stability of reactive phases in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ are described. Future plans for equilibrium studies and for glass corrosion studies are presented.

I. INTRODUCTION

This report covers the work completed under contract BNL 418691-S during the fifth quarter of research from July 1, 1978 to September 30, 1978. The research was concentrated on three areas. The first involved a continuation of the glass corrosion work. The second extended the work on the stability of potential cementing phases in the $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ quaternary system and the third area involved the cement formation of mixtures of Al_2O_3 and phosphoric acid.

II. THE CORROSION OF GLASSES

The importance of the interaction of calcium aluminosilicate glasses with phosphoric acid for controlling setting times of potential cements has been discussed in previous reports. Essentially, the silicate glass is used to hold reactants which form a cement when they react with phosphoric acid. The setting time of the cement depends upon the rate at which the reactants are released from the glass by acid attack.

Thus far, the glasses studied contain equal weight percentages of calcium oxide and aluminum oxide with silica content varying from 40 weight percent to 65 weight percent. A mixture such as 30 CaO :30 Al_2O_3 :40 SiO_2 is melted in a platinum crucible and stirred for homogeneity. Fibers are drawn from the melt, checked for uniformity and cut into one inch lengths and used for corrosion studies. The technique

used for the original measurements has been described in previous reports. The technique has the drawback that each data point represents a different fiber. Since each fiber must be weighed separately and surface measurements must also be done, the method is time consuming and tedious.

For the above reasons, a new method was attempted this quarter and is yielding meaningful results. It is a continuous weight change method. A single fiber is held in a sling with a platinum wire. The fiber is submerged in a phosphoric acid bath inside an oven. A balance is placed on top of the oven and the platinum wire holding the fiber is attached to the balance through a hole in the top of the furnace. Weight loss readings are made continuously. Thus, one fiber gives hundreds of data points. The reading obtained is not the weight loss of the fiber but rather the weight loss plus the change in buoyancy resulting from the reduced fiber volume. This method is not usable if a silica film is produced on the fiber because the buoyancy can not be determined because of the unknown density of the silica gel phase which occurs on some fibers. An important part of each run is a microscopic investigation to determine if a gel layer is produced on the glass surface. The glasses which have been examined thus far by the first method are the following:

17.5 CaO:17.5 Al₂O₃:65 SiO₂,
21.5 CaO:21.5 Al₂O₃:57 SiO₂,
22.5 CaO:22.5 Al₂O₃:55 SiO₂,
23.5 CaO:23.5 Al₂O₃:53 SiO₂,
25 CaO:25 Al₂O₃:50 SiO₂, and
30 CaO:30 Al₂O₃:40 SiO₂

All of the numbers are given in weight percent. The data presented in this report were all obtained by the first method. Runs are currently being made by the second method and will be presented in the next report.

Determinations on the 55, 57 and 65% silica fibers showed an interaction with the 30 percent phosphoric acid below the level of detection (<0.5 mg) for both 40°C and 90°C. The fibers also do not show any signs of interaction with the acid. The 40, 50 and the 53% SiO₂ glass lose weight linearly.

Figs. 1 and 2 show the loss in weight/surface area for the 53% fibers at 40°C and 90°C respectively while Figs. 3 and 4 show the data for the 40% glass. A hydrated silica gel layer is observed on the 53% glass; the 40% glass dissolves without any film formation.

Fig. 5 shows a 53% glass fiber seen under the microscope after immersion in the acid for 64 hours at 40°C. The unattacked glass and the film formed on it are visible. Fig. 6 shows a fiber of the same glass after 128 hours at 40°C. The unattacked glass has become very thin. If the fiber had been in the acid for some more time there would not have been

Figure 1. Weight loss of 53% SiO₂:23.5% CaO:23.5% Al₂O₃ glass.

Figure 2. Weight loss of 53% SiO₂:23.5% CaO:23.5% Al₂O₃ glass.

Figure 3. Weight loss of 40% SiO₂:30% CaO:30% Al₂O₃ glass.

Figure 4. Weight loss of 40% SiO₂:30% CaO:30% Al₂O₃ glass.

Figure 5. Corroded 53% SiO₂ fibers. Gel film on unaffected glass core after 64 hrs at 40°C.

Figure 6. Corroded 53% SiO₂ fibers. Gel film on unaffected glass core after 128 hrs at 40°C.

any bulk glass left. At 90°C, there is no bulk glass left after 5 hours and so the graph in Fig. 2 tends to flatten out.

It has not been determined whether the silica gel phase dissolves very slowly in phosphoric acid. If it does, the high weight loss curve will be followed by a low weight loss curve.

For the 53% silica glass at 90°C, a measurement was made of the change in thickness of the bulk glass with time. The decrease in thickness was obtained by taking the difference of the initial thickness and the fiber thickness after the film was scraped off. This data is plotted as a function of time in Fig. 7. This measurement gives a linear corrosion rate as does the weight loss data. The fiber shows a decrease in thickness only after a certain time has elapsed indicating that there is some incubation time involved.

For 40% SiO_2 glass the experimental runs were repeated several times for both the temperatures. For any given time a fiber was immersed in the acid, a scattering in the weight loss data were noted. Thus, for the correct interpretation of the results a statistical analysis of the data were made.

The best fitting line is obtained by the method of least squares. This is the line plotted in those figures. The slope and the intercept of the line are obtained by using a computer program for statistical analysis of data called

"Stat-pack." A positive intercept at zero time could be due to a parabolic dissolution rate for a very short initial period. A printout obtained for the 40% SiO_2 glass at 90°C is shown in table 1.

Figs. 8 and 9 plot the weight loss data for the different composition glasses on the same scale at 40°C and 90°C respectively. This enables us to compare the effect of temperature and SiO_2 composition. The y-axis in both the figures has the same scale while the x-axis (i.e. time axis) is much smaller for the graph at 90°C. This comparison gives some indication of the effect of temperature on the dissolution rate.

Figure 10 summarizes the data presented in the above plots. The corrosion rates (wt loss/surface area x time) are plotted as a function of silica concentration. Data on the 50% silica glass have been contradictory and further determinations are being made. There is a dramatic change in solubility at both 40°C and 90°C between the 55% silica glass, which shows essentially no corrosion and the 53 and 40% silica glasses.

Previous reports have postulated a change in the solubility due to a decrease in the degree of polymerization of silica tetrahedra as the calcium ion and aluminum ion concentration increases in the glass. While this theory may prove to be correct, it is more likely that such a polymerization change would produce a continuous increase in solubility. The change in corrosion rates observed appears to be almost a step change

TABLE 1. PRINT-OUT FOR STATISTICAL ANALYSIS OF CORROSION DATA

THU 24 AUG 78 LINE 05
USER NUMBER: PACEWORK
000001:00000000
READY
RUN STATPACK

STATPACK 15115 THU 24 AUG 78

ARE YOU A STATPACK EXPERT
?# NO

THE RESPONSE "YES" MAY BE ENTERED IN ORDER TO GAIN ADDITIONAL INFORMATION ABOUT THE RESPONSE NEEDED BY STATPACK. YOU MAY RE-ENTERED ONLY IF THE QUESTION IS FOLLOWED BY THE CHARACTER "Y"

SPECIFY THE NAMES OF THE INPUT AND OUTPUT FILES (FORMIN, ONLY)
?# 0.0

WHAT ANALYSIS DO YOU WISH TO PERFORM
?# REGRESSION

HOW MANY ROWS IN YOUR DATA MATRIX
?# 24

HOW MANY COLUMNS
?# 2

NUM. ENTER EACH ROW
?# 0.000000

?# 0.010000

?# 0.014100

?# 0.022000

?# 0.025000

INPUT DATA NOT IN CORRECT FORMAT, RETYPE IT.

?# 0.026000

?# 0.040000

?# 0.045000

?# 0.046000

?# 0.047000

?# 0.048000

?# 0.049000

?# 0.050000

?# 0.051000

?# 0.052000

?# 0.053000

?# 0.054000

?# 0.055000

?# 0.056000

?# 0.057000

?# 0.058000

?# 0.059000

?# 0.060000

?# 0.061000

?# 0.062000

?# 0.063000

?# 0.064000

?# 0.065000

?# 0.066000

?# 0.067000

?# 0.068000

?# 0.069000

?# 0.070000

?# 0.071000

?# 0.072000

?# 0.073000

?# 0.074000

?# 0.075000

?# 0.076000

?# 0.077000

?# 0.078000

?# 0.079000

?# 0.080000

?# 0.081000

?# 0.082000

?# 0.083000

?# 0.084000

REGRESSION COEFFICIENTS 0.000000

STD. ERROR OF EST. COEFF. 0.150000

CORRELATED COEFF. 0.999000

CORRELATION COEFF. 0.999000

STANDARD ERROR OF ESTIMATE 0.150000

ANALYSIS OF VARIANCE FOR THE REGRESSION

SOURCE OF VARIATION	D.F.	SUM OF SQ.	MEAN SQ.	F VALUE
REGRESSION	1	0.999000	0.999000	215.972
DEVIATION FROM REGRESSION	23	0.001000	0.000043	
TOTAL	24	1.000000		

DO YOU WISH TO PRINT THE TABLE OF RESIDUALS
?# YES

CASE NO	Y OBSERVED	Y ESTIMATED	RESIDUAL	STD. RESID.
1	0.610000	0.609000	-0.000000	-0.000000
2	0.110000	0.110000	0.000000	0.000000
3	0.140000	0.140000	0.000000	0.000000
4	0.220000	0.220000	0.000000	0.000000
5	0.260000	0.260000	0.000000	0.000000
6	0.340000	0.340000	0.000000	0.000000
7	0.270000	0.270000	0.000000	0.000000
8	0.460000	0.460000	0.000000	0.000000
9	0.170000	0.170000	0.000000	0.000000
10	0.100000	0.100000	0.000000	0.000000
11	0.150000	0.150000	0.000000	0.000000
12	0.240000	0.240000	0.000000	0.000000
13	0.230000	0.230000	0.000000	0.000000
14	0.260000	0.260000	0.000000	0.000000
15	0.330000	0.330000	0.000000	0.000000
16	0.400000	0.400000	0.000000	0.000000
17	0.790000	0.790000	0.000000	0.000000
18	0.120000	0.120000	0.000000	0.000000
19	0.160000	0.160000	0.000000	0.000000
20	0.210000	0.210000	0.000000	0.000000
21	0.300000	0.300000	0.000000	0.000000
22	0.340000	0.340000	0.000000	0.000000
23	0.390000	0.390000	0.000000	0.000000
24	0.450000	0.450000	0.000000	0.000000

TEST OF EXTREME RESIDUALS
RATIO OF RANGES FOR THE SMALLEST RESIDUAL..... 0.029
RATIO OF RANGES FOR THE LARGEST RESIDUAL..... 0.171
CRITICAL VALUE OF THE RATIO AT ALPHA = .10 ... 0.367

DO YOU WISH TO PLOT Y OBSERVED AND Y ESTIMATED
?# YES

TYPE PRINT CHARACTERS FOR Y OBSERVED AND Y ESTIMATED IN THE FORM X,Y
YU,L

INPUT DATA NOT IN CORRECT FORMAT, RETYPE IT.
?#

INPUT DATA NOT IN CORRECT FORMAT, RETYPE IT.
?#E

DO YOU WISH TO KEEP ANY RESIDUALS
?# NO

DO YOU WISH TO COMPUTE THE DISPERSSION STATISTIC
?# NO

DO YOU WISH TO COMPUTE MORE REGRESSION
?# NO

DO YOU WISH TO PERFORM OTHER ANALYSIS
?# NO

THIS IS NOT AVAILABLE. TRY TO NAME AGAIN CORRELATED
?# FINISH
END OF RUN

Figure 7. Decrease in fiber thickness of bulk glass.

Figure 8. Weight loss of compositions studied.

Figure 9. Weight loss of compositions studied.

Figure 10. Corrosion rates of glasses studied.

and it occurs close to 50% SiO_2 .

An explanation of such a step change can be found in the spinodal decomposition theory of glass proposed by Cahn and Charles. The theory states that over certain ranges of composition, a quenched glass, which is a metastable liquid, becomes unstable and breaks down, without nucleation and growth, into two immiscible glass phases. If the calcium aluminosilicates undergo spinodal decomposition the cooled fibers would be made up of submicroscopic droplets of one glass phase in a matrix of the predominant second glass phase. The two glass phases formed by spinodal decomposition would most likely be a silica rich phase and a calcium aluminate phase. The silica rich phase would show essentially no corrosion in phosphoric acid. The calcium aluminate phase would be extremely soluble even in water.

The observed corrosion rates can be explained by such a theory in the following manner. Fibers richer in silica than 50% separate on cooling into two phases. The insoluble silicate glass is dominant and forms a matrix which contains units of dispersed aluminate phase. Since the matrix is insoluble and the soluble phase is isolated from the corroding liquid by the silicate phase, a zero corrosion rate is observed. When the fiber composition is moved to silica concentrations less than 50% the matrix phase is an aluminate which is extremely soluble. The dispersed phase is droplets of silica. On exposure to acid, the aluminate dissolves and the silica units go into colloidal suspension. The dissolution

rates for the glasses will be either zero or very high. A transition fiber is observed by us at 53% silica. This is the phase that shows a silica film. The composition represents a point where neither aluminate or silicate are the dominant phase but both are continuous. The acid dissolves away the aluminate leaving a siliceous layer on the surface of the fiber.

The size of the dispersed phase is smaller than the wave length of visible light. If this were not so, the fiber would become white as the dispersed phase scattered the light. The fibers remain optically clear. Fibers are being prepared for electron microscope examination. It may be possible to see the dispersed phase by these techniques. Spinodal decomposition theory would predict a dispersed phase size of about $100\text{\AA}$. This size can be increased by proper heat treatment. Some experiments will be tried to see if the heat treatment range can be found.

III. EQUILIBRIUM STUDIES

Experiments are continuing to determine which phases are stable at temperatures and water-vapor partial pressures which may be encountered at geothermal conditions. The current experiments are centered in three areas. The first set is examining the reactions of $\text{Al}(\text{OH})_3$ and Al PO_4 to determine if a stable solid solution series exists between Al PO_4 and Gibbsite. These runs have been completed and the phases present after 100 days are being determined.

The second set of experiments is aimed at determining if augellite will act as a cementing phase. Three dry powder mixtures of Al_2O_3 and Al PO_4 were made up to act as cement powders. Each of these powders was mixed with different liquids. Three liquids were used - pure water, 30% phosphoric acid and 50% phosphoric acid. The powders and liquids were mixed to form a paste and the paste was sealed in pyrex tubing which was subsequently placed in a furnace at 200°C . Data on the phases present, volume changes and cement formation are currently being determined and will be reported in the January quarterly report. All cements were designed to have augellite as the cementing phase. That augellite will form can be predicted from the previous equilibrium work on the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. The question which must be answered by these experiments, however, is whether or not the phase will be a cementing phase. A dry friable unbonded powder could result.

The final set of equilibrium experiments being conducted at this time involves the determination of phases which will be stable under geothermal conditions in the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. All runs are being made at 200°C in closed pyrex containers. Three calcium aluminates are being reacted with the following phosphoric acids: 90 H_2O :10 P_2O_5 , 70 H_2O :30 P_2O_5 and 50 H_2O :50 P_2O_5 . The results of these experiments will also be discussed in the next quarterly report.

IV. FUTURE PLANS

1. The corrosion of the calcium aluminosilicate glasses will be completed during the next quarter.

2. The addition of sodium oxide to lower the melting point of the calcium aluminosilicates will be made. Fibers will be drawn and the corrosion rates will be determined.

3. The sodium-calcium-aluminum-silicate glasses will be reacted with phosphoric acids to determine if cements form. If they form, they will be subjected to stability tests at 200°C.

4. Work will continue on the $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ system to determine if any quaternary phases exist which are stable at elevated temperatures and could act as a cementing phase.

APPENDIX 6

COMPRESSIVE, TENSILE, PIPE-BONDING STRENGTHS, AND PERMEABILITY OF SELECTED
CEMENTING-MATERIALS FOR HOT-DRY-ROCK WELLS

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Prepared for:

Cementing of Geothermal Wells
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Abstract

Compressive and tensile strength data for five cementing-materials, which are candidates for cementing hot-dry-rock wells, were obtained after 40 and 176 hour exposure to water in an autoclave at 195 °C (383 °F) and 21 MPa (3000 psi). Additional tests will be conducted after extended exposure of four and eight weeks to similar conditions; these exposures are presently two weeks underway.

In addition, an apparatus is under construction, and specimens are being prepared, to measure at ambient laboratory conditions the shear bond strength of the interface between a cementing-material and a steel rod, and the permeability to water of a cementing-material. We also plan to investigate the effect that thermal cycling between autoclave conditions and ambient laboratory conditions will have on these properties.

Introduction

NBS was requested to participate in a special test program that would provide data for use in the selection of a material to cement hot-dry-rock wells located at the Los Alamos Scientific Laboratory [1]. As part of this program we have agreed to measure some strength properties of several cementing-materials at ambient laboratory conditions after they have been exposed to high-pressure water near 200 °C for one, four, and eight weeks, and after they have been thermally cycled between these exposure conditions and ambient laboratory conditions. As part of a general program, we have been constructing over the past several months a test facility in which strength properties will be determined for cementing-materials that are candidates for application in geothermal wells. In this facility, whose completion has been deferred until November to obtain the present data, cementing-materials will be exposed to geothermal fluids up to 400 °C (750 °F) and 70 MPa (10,000 psi). Fortunately, in regard to the cements for the hot-dry-rock application, we were able to utilize a recently installed, one gallon, stirred autoclave which is operational up to 340 °C (650 °F) and 21 MPa (3000 psi).

By the last week of August we had received five different cementing materials from four suppliers [2, 3, 4, 5]. Our time schedule in testing these materials was delayed, however, due to the difficulty in obtaining samples of adequate setability, and/or strength, for three of these materials. In one case the original formulation provided by the supplier [3] resulted in an unsettable cement; but by reducing the amount of retarder, under the advice of the supplier, a successful cement formulation was obtained on the third attempt. In the other two cases, strengths

indicated by the supplier [4] were not obtained after two separate trials on each. This supplier suggested that segregation of the dry components in the pre-mixed stock may have prevented the selection of a representative sample, thus resulting in the lower strength values. Smaller batches, which will be used in their entirety, are being formulated by the supplier to rectify this problem.

Sample Preparation

The source of supply and formulation (mass ratio of components) of each of the five cementing-materials tested in this investigation are indicated below:

A. class G cement silica: [reference 2], 1.0 API class G cement, 0.4 silica flour (200 mesh), 0.6 distilled water (Table 14.2 of reference 7);

B. class H cement/silica/retarder: [reference 3 (revised formulation)], 1.0 API class H cement, 0.35 silica flour, 0.025 D13 (lignin), 0.025 D93 (borax), 0.45 distilled water;

C. zinc oxide cement: [reference 4], 1.0 powdered mix provided by supplier. 0.18 water provided by supplier;

D. aluminum hydroxide cement: [reference 4], 1.0 powdered mix provided by supplier, 0.18 water provided by supplier; and

E. polymer cement: [reference 5], 0.3 Portland Type III cement, 0.7 sand mix (0.35 no. 16 mesh, 0.175 no. 30 mesh, and 0.175 no. 100 mesh), 0.13 liquid monomer mix (0.065 styrene, 0.0455 acrylonitrile, 0.013 divinyl benzene, and 0.0065 acrylamide), 0.0013 A-174 silane, and 0.00065 AIBN catalyst.

right circular cylindrical samples used, had a nominal 9 mm radius $\underline{r}$ and a length $\underline{\ell}$ which was nominally four times the radius for a compressive strength test and equal to the radius for a tensile strength test. From the load $\underline{F}$ required to break a sample, the compressive strength $\underline{S_c}$ and the tensile strength $\underline{S_t}$ were calculated from

$$S_c = F_c / \pi r^2 \quad \text{and}$$

$$S_t = F_t / \pi r \ell, \quad \text{respectively.}$$

A universal testing machine of 12,000 lb capacity was used to apply the load with a displacement rate of about 0.5 mm/min. The results of these tests are given in the following table.

Table 1. Compressive strength $\underline{S_c}$ and tensile strength $\underline{S_t}$ of geothermal cementing-materials after exposure to water in an autoclave at 195 °C and 21 MPa. Entries are the mean value and standard deviation for five specimens.

Cementing Material ^(a)	$\underline{S_c}$ /MPa		$\underline{S_t}$ /MPa	
	40 h	176 h	40 h	176 h
A	90.4 $\pm$ 8.5	63.7 $\pm$ 6.4	9.36 $\pm$ 1.05	7.75 $\pm$ 0.36
B	102.1 $\pm$ 10.4	71.1 $\pm$ 4.9	12.46 $\pm$ 0.28	9.77 $\pm$ 1.05
C	34.0 $\pm$ 3.4	4.0 $\pm$ 1.4	4.95 $\pm$ 0.64	0.83 $\pm$ 0.15
D	15.8 $\pm$ 3.7	20.3 $\pm$ 6.3	2.58 $\pm$ 0.62	3.03 $\pm$ 0.74
E	172.3 $\pm$ 1.8 ^(b)	177.6 $\pm$ 2.4	28.2 $\pm$ 1.3 ^(b)	19.7 $\pm$ 2.6

(a) See text for identity and source.

(b) Cured as described in text, but not exposed in the autoclave.

Using 0.6 kg batches of dry components, we prepared slurries of the cementing-materials A, B, C, and D. The first two materials were mixed with water for 40 s in a blender [6]. Being considerably more viscous the last two materials were mixed with water for 10 min in a mixer [4]. These slurries were poured into Pyrex tubes (20 mm OD by 150 mm) coated inside with a silicone grease, puddled with a rod to remove air bubbles, and capped with Teflon plugs. These materials were cured under water in an autoclave at 195°C and 21 MPa for 40 hour, as measured from start-to-heat to start-to-cool. Approximately one hour was required both to heat and to cool the previously pressurized autoclave. In contrast, a slurry of cementing-material E was prepared by the supplier with 0.3 kg batches of dry components [5]; the ingredients were preheated to 55°C before mixing by hand, poured into Pyrex tubes coated inside with a release agent, vibrated to remove air bubbles, and cured at one atmosphere in an oven at 55°C for 4 h, then at 110°C for 18 h.

After all the cementing-materials were set and cooled to ambient laboratory conditions, the thin-walled Pyrex tube molds were broken away, and samples of the cementing materials were cut to size with a diamond saw. Except for those samples set aside for the initial strength tests, the remaining samples of all the cementing materials were packed together in the autoclave for extended exposures to water at 195 °C and 21 MPa.

Strength Measurements

We decided to measure not only the customary compressive strength, but also a tensile strength by diametral compressive loading [8]. The

Although the compressive strength values of cementing-materials A and B appear to decrease with time of exposure to the autoclave conditions, these values still exceed by roughly one-third the values reported for a similar cementing-material under almost the same autoclave conditions [9]. In the case of cementing-material B, however, roughly 10 per cent of the top portion of the cured material did not set and remained mushy. In two earlier formulations of this material, in which the proportion of retarder was greater (as specified by the supplier [3]) the whole sample in the mold failed to set and remained mushy.

In the first preparation of cementing-material C, being cured under autoclave conditions for 24 h, the set samples were so fragile that they could not be removed from the molds without fracturing the specimen. Increasing the curing time to 40 h, however, provided a satisfactory strength for removal from the mold. Although this material seemed to have an initial compressive strength comparable to that reported [4] by its supplier, the compressive strength dropped to about one-tenth of the expected value [4] after 1 wk exposure. Samples of cementing-material D were difficult to remove from their molds even after a 40 h exposure time, and the compressive strength was observed to be about half the expected value [4]. As mentioned above, the supplier suggested that these anomolous effects may have resulted from a segregation of the dry components so that a unrepresentative sample was prepared.

Future Plans

We plan to repeat the above strength tests on new formulations of cementing materials C and D when a replacement stock of pre-mixed powdered batches are received. To avoid the possibility of segregation, we will

use each pre-mixed batch in its entirety with the appropriate amount of water. Additional strength tests on samples of the cementing-materials reported in Table 1 will also be made after they have been exposed for the extended periods of 4 and 8 weeks. These exposures are presently two weeks underway.

We plan to investigate the effect that thermal cycling between autoclave conditions and ambient laboratory conditions will have on certain properties of the cementing-materials. The shear-bond strength of the interface between a cementing-material and a steel rod will be determined by measuring at room conditions the force required to initiate movement of the rod in the area of a cement sheath. The permeability to water of a cementing-material will be determined by measuring at ambient laboratory conditions the exponential decay of the pressure difference of water across a given volume of sample. Special sample-holding fixtures are being fabricated, and other parts have been ordered to construct the apparatus. Samples will be cured in their fixtures while being exposed to water near 200°C and 14 MPa (2000 psi) in an autoclave.

In regard to the shear-bond strength, we recognize that the strength value is particularly sensitive to the surface finish of the steel rod. The shear-bond strength between a clean non-varnished cold-rolled steel and an API class A cement, which has been cured for one day at 80°F and one atmosphere, was reported [10] to have a value near 0.72 MPa, whereas a sand-blasted and resin-coated surface finish was reported to give a value of 17 MPa. After consulting with Dr. Roland A. Pettitt at Los Alamos Scientific Laboratory, we have agreed to use a clean non-varnished cold-rolled steel rod because this will give a reproducible and representative surface finish.

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