CEMENTING OF GEOTHERMAL WELLS

PROGRESS REPORT NO. 12
JANUARY - MARCH 1979

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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 January 1 - March 31, 1979 is described in the current report.

Summary

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

The second meeting of the American Petroleum Institute's (API) Task Group on geothermal cements which serves as a review group for the DOE/DGE program, was held on January 24-25, 1979. The third meeting is scheduled for June 19, 1979.

Phase II of Dowell's program is continuing. Field tests are in progress at East Mesa and Niland. Results from initial tests in the Dynamic Brine Exposure Testing Apparatus (D-BETA) are available. Based upon initial data, the rate at which cement coupons undergo change in the D-BETA is between that of the static tests and the dynamic exposures at East Mesa. Systems that were strong upon static exposure were able to maintain strength when dynamically treated. Conversely, cements that were weak when statically tested tended to be weaker still after dynamic exposure.

At Battelle's Columbus Laboratories several cementing compositions have been formulated with chemical, physical and mechanical properties to withstand the existing geothermal conditions. The pumpability of three formulations has been demonstrated and the materials have been submitted to NBS for additional evaluation.

The effects of Al_2O_3 , Fe_2O_3 , SO_3 , Na_2CO_3 and Na_2SO_4 on different binders were studied at Colorado School of Mines. The results were found to range from deleterious to beneficial. Aluminous tobermorite, xonotlite, and truscottite were dominant ultimate binders. The present results and others indicate that truscottite may undergo serious strength retrogression upon long-term exposure. A-Tobermorite was stable to 250°C or higher. Xonotlite exhibited a wide range in

strength, and some limited evidence suggests that it too may undergo strength retrogression. No insurmountable difficulties were encountered with normal-weight cements, but light-weight cements posed some questions.

Phosphate-bonded cements have been produced at the University of Rhode Island from a glass containing 7% Na_2O , 24% CaO , 24% Al_2O_3 and 45% SiO_2 . Preliminary tests indicate that the material sets in several hours and appears to have some high temperature stability.

Tests performed on hydrothermal cements developed at Southwest Research Institute indicate six formulations that are pumpable as long as three hours at 316°C . Two formulations, Al_2O_3 and ZrO_2 have been chosen for use at temperatures above 300°C .

Polymer concretes containing cement fillers have been found to be hydrothermally stable in 300°C brine. The optimum cement concentration is in the range 15 to 18 wt%. Over the temperature range 25° to 350°C , the compressive strength of one formulation is essentially constant at ~ 72 MPa.

Recommended standards for evaluating geothermal well cements have been developed by NBS. Review by the API Task Group is in progress.

Cementing of Geothermal Wells

Progress Report No. 12

January-March 1979

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.

Goal No. 1 has been attained. The other goals will be 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.

Work is currently being performed in Tasks 1, 3, 5 and 6. Contingent upon the availability of funding, work will commence on Tasks 2 and 4.

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 twelfth in a series of quarterly reports describing work on the program. Accomplishments during the period January-March 1979 are summarized below.

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 (approximately 10 yr) application should be given to medium salinity brines at temperatures up to 400°C.

In an earlier report,¹ an outline of the approved management plan was presented. The program consists of the following elements: problem definition, materials development, property verification, down-hole testing, and the use of the cements in completing demonstration wells. The problem definition element has been completed and work is progressing in the materials development and property verification phases. Pumpability tests have been performed on several promising cement systems. 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

The experimental phase of the Colorado School of Mines program was completed in September 1978 and the final report has been written. All other parts of the materials development phase with the exception of the Dowell work will be completed by September 30, 1979.

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 Mr. H.J. Beach of the Gulf Research and Development Company. Mr. J.P. Gallus of Union Oil of California is Chairman of the Task Group. The second meeting of the Task Group was held in Houston, Texas on January 24-25, 1979. The minutes for the meeting and a list of attendees are given in Appendix 1. The next meeting of the task group will be held in conjunction with the API Standardization Committee meeting in San Diego on June 19, 1979.

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

Styrene (St) - Acrylonitrile (ACN) - Acrylamide (Aa) - Divinyl Benzene (DVB) Copolymers

A simplified method for producing PC containing the monomer mixture has been developed. In previous work it was necessary to heat the monomer mixture to 45° to 50°C prior to mixing with the inorganic filler in order to dissolve the solid Aa. In an attempt to eliminate the heating requirement, tests were performed in which the Aa was included as a partial constituent of the aggregate. After mixing the aggregate with the other monomer constituents, the formulation was cured by use of an initiator (azobisisobutyronitrile) and heating to 60°C.

Infrared (IR) and TGA evaluations indicated that both fabrication methods yield copolymers with the same chemical structure.

Compressive strength measurements performed at different temperatures on specimens prepared by each of the methods have also given similar results. The data, given in Figure 1, are for samples containing 11.5 wt% monomer (50 wt% St - 35 wt% ACN - 5 wt% Aa - 10 wt% DVB), 62 wt% silica sand and 26.5 wt% Type III portland cement.

Organosiloxane (OS) Polymers

A study to evaluate the effect of the cement filler composition on the properties of PC containing a 97 wt% RZ - 3 wt% V47 organosiloxane mixture has been completed. Samples were exposed to a 25% brine solution at 300°C for 60 days and the test results are summarized in Figures 2-6. The results indicate that the PCs are thermally and hydrolytically stable and that the optimum cement concentration is in the range 15 to 18 wt%. Data given in Figure 7 indicate that over the temperature range 25° to 350°C, the compressive strength of one composite formulation is essentially constant at a value of ~ 72 MPa.

A study has been started to further improve the mechanical properties of PCs containing the RZ-V47 organosiloxane mixture. In this work various additives are being included in the inorganic phase and the effects on hydrothermal stability determined. The data, given in Figure 8 and Table 1, are summarized in terms of a strength factor (α).

$$\alpha = \frac{\partial_1}{\partial_0}$$

where

∂_1 = strength after exposure to brine at 300°C.

∂_0 = initial strength.

The results to date indicate that the inclusion of MgSiO_3 , CaSiO_3 and Fe_2O_3 improves the hydrothermal stability of the composite by significant amounts. This work is being continued.

It is well known that the introduction of polar groups into the molecular chain will increase the thermal stability and the adhesion coefficient of organosiloxane polymers. Tests have been performed on

Figure 1. Compressive strength of St, ACN, Aa, and DVB polymer concrete at various temperatures. Preparation method: Δ, Aa added as a solid to filler. X, Aa dissolved in other monomers prior to mixing with filler.

Figure 2. Compressive strength and absorption of OS PCs after exposure to brine at 300°C. OS composition, 97% RZ - 3% V47. Aggregate composition, 90% sand - 10% cement. I, Type I portland cement; II, Type II portland cement; III, Type III portland cement; V, Type V portland cement.

Figure 3. Compressive strength and absorption of OS PCs after exposure to brine at 300°C. OS composition, 97% RZ - 3% V47. Aggregate composition, 95% sand - 5% cement. I, Type I portland cement, II, Type II portland cement, III, Type III portland cement, V, Type V portland cement.

Figure 4. Compressive strength and absorption of OS PCs after exposure to brine at 300°C. OS composition, 97% RZ - 3% V47. Aggregate composition, 80% sand - 20% cement. I, Type I portland cement; II, Type II portland cement; III, Type III portland cement; V, Type V portland cement.

Figure 5. Compressive strength and absorption of OS PCs after exposure to brine at 300°C. OS composition, 97% RZ - 3% V47. Aggregate composition, 80% sand - 20% cement. I, Type I portland cement; II, Type II portland cement; III, Type III portland cement; V, Type V portland cement.

Figure 6. Compressive strengths of OS PCs, after exposure to brine at 300°C, as a function of cement type and concentration. Summary of results.

Figure 7. Compressive strength of OS PC as a function of temperature. OS composition, 97% RZ - 3% V47. Aggregate composition 90% sand - 10% Type V portland cement.

Figure 8. The effect of additives on the hydrolytic stability of OS PCs after exposure to brine at 300°C for 30 days.

Table 1

Strength Factors for OS PC Containing Additives after Exposure to Brine at 300°C

<u>Additive</u>	<u>MgSiO₃</u>			<u>CaSiO₃</u>			<u>Fe₂O₃</u>			<u>Mica</u>			<u>Carbon Black</u>	
Concentration, wt%	<u>2</u>	<u>4</u>	<u>6</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>2.5</u>	<u>1.0</u>
Strength Factors														
α_1	1.02	0.76	1.17	1.31	0.79	1.06	1.01	0.96	0.54	0.84	0.87	0.55	0.52	1.16
α_2	0.72	--	1.15	0.5	1.11	--	0.61	1.16	0.51	0.70	0.96	0.51	0.37	0.76

α_1 , after 30 days in brine at 300°C.

α_2 , after 60 days in brine at 300°C

Without additives, $\alpha_1 = 0.89$

$\alpha_2 = 0.61$

copolymers containing 97 wt% RZ and 3 wt% ACN. In a nitrogen atmosphere, the copolymer is stable up to a temperature of 400°C. Additional work in this area is planned.

Vinyl-Type Polymers

In an earlier report,² it was described that the addition of tricalcium silicate (abbreviated form C₃S) to vinyl-type PC results in mechanical and physical properties greater than those obtained from PC containing calcium carbonate, calcium hydroxide and silica flour. The results suggested that the presence of C₃S has two significant effects which tend to improve the strength and durability of PC in hot brine. The first is due to the hydration products of C₃S formed during exposure to hydrothermal conditions, and the second is due to a chemical reaction between the C₃S and the polymer.

During the current period, data regarding the effect of the reaction products on the hydrothermal stability have been obtained and a proposed reaction mechanism developed.

Polymethylmethacrylate (PMMA) was selected for use as a binder in this study and reactions between it and C₃S during exposure to brine at 240°C were evaluated. IR, TGA, DTA and mechanical tests were performed.

Results of the IR analysis are shown in Figures 9 and 10. As shown in Figure 9, the IR spectra of anhydrous C₃S is characterized by a wide absorption band occurring around 840 cm⁻¹. IR absorption bands (sample No. b) of C₃S-filled PMMA samples before exposure to brine indicate a symmetric stretching vibration of CH₂ groups at 2940 cm⁻¹, a stretching vibration of C=O groups at 1710 cm⁻¹, an asymmetric and symmetric deformation vibration of CH₃ groups at 1420 cm⁻¹, and at 1130 cm⁻¹ a band which may be due to an asymmetric vibration of the C-O-C group.

In Figure 10, the spectra (sample No. c) for C₃S-filled PMMA samples after exposure for 10 days to hot air at 240°C was observed to be similar to that of the control sample. This curve seems to demonstrate that an interaction of C₃S with PMMA molecules does not occur when the sample is exposed to hot air. The C₃S pastes were prepared with a water to C₃S ratio of 0.35, and subsequently cured under water for 7 days at 25°C. The IR spectra for the cured C₃S specimen

Figure 9. Infrared spectra of anhydrous C₃S and C₃S-filled PMMA: a, anhydrous C₃S grains, b, C₃S-filled PMMA before exposure to brine.

Figure 10. Infrared spectra of hydrated C₃S and C₃S-filled PMMA after exposure to hot air and hot brine: c, C₃S-filled PMMA after heating in dry oven, d, hydrated C₃S after exposure to hot brine, e, C₃S-filled PMMA after exposure to hot brine.

after exposure for 10 days to brine at 240°C is represented by the curve for sample No. d. This curve has four major absorption bands due to the C₃S hydrate at 3400, 1440, 1195, and 960 cm⁻¹. This spectra also indicates that the hydration products of C₃S can be recognized from the disappearance of the anhydrous C₃S band at 840 cm⁻¹. The IR spectra for C₃S-filled PMMA after exposure to brine (sample No. e) illustrates a very interesting curve; namely, the two new bands at 1540 and 1398 cm⁻¹. These bands represent an asymmetric stretching vibration and a symmetric stretching vibration of the COO⁻ (Ca) group, respectively, which are due to an ionic bond between Ca²⁺ ions and carboxylate anions (COO⁻) which developed during exposure to the hydrothermal conditions. It is believed that these bands correspond to the results reported by Leyte et al.³ and Crisp et al.⁴ for the IR studies of the interaction between metal oxides and an aqueous solution of polyacrylic acid.

The chemical reaction mechanisms occurring at the interface between PMMA and C₃S grains are believed to be represented by a reaction process as shown in Figure 11. As indicated in the figure, Ca²⁺ ions are released readily by the attack of the hot brine on the anhydrous C₃S grains. These Ca²⁺ ions produced in a aqueous media develop an electrostatic interaction with the carbonyl groups (-C=O⁻) which become more strongly electropositive by the elevated temperature. Thus the carboxylate group can be changed easily to the carboxylate ion (-COO⁻) by the electrostatic interaction. The chemical effect of Ca²⁺ ions may be presumed to be a cross-linking function which connects two -COO⁻ groups between PMMA chains and within a single chain.⁵⁻⁷ A partial Ca-PMMA complex is covered with hydration products of C₃S which form under the conditions of high temperature and pressure in the autoclave.

The thermal stability of the Ca-PMMA complex produced by the ionic bonding of Ca²⁺ ions with carboxylate (COO⁻) ions was investigated by TGA and DTA analysis.

As shown in Figure 12, the TGA curve of the Ca-PMMA complex indicates that the loss of material begins to occur slowly at approximately 300°C, exclusive of the weight decrease occurring rapidly in the range 40° to ~ 150°C which is probably due to vaporization of

Figure 11. Reaction mechanisms between C_3S and PMMA during exposure to brine.

neutral H_2O molecules co-ordinated to Ca^{2+} ions in Ca^{2+} bridges.⁸ The temperature at which $\sim 25\%$ weight loss of the complex occurs is about $570^\circ C$. Compared to the onset temperature of thermal decomposition obtained from the TGA curve for the Ca-PMMA complex, the thermal decomposition of C_3S -filled PMMA samples before exposure to brine occurs gradually around $200^\circ C$. This is $\sim 100^\circ C$ lower. This curve also indicates that the weight loss of 25% of product takes place at about $390^\circ C$.

From the DTA thermogram in Figure 12 of the Ca-PMMA complex, it can be seen that a large exothermal peak occurs at about $480^\circ C$ at the same time that the thermal degradation of the unexposed complex shows to be almost finished. The broad exothermal peak at about $80^\circ C$ is probably a result of the influence of neutral H_2O molecules co-ordinated to those Ca^{2+} ions in Ca^{2+} bridges, as described in the TGA curve. On the contrary, the thermogram of C_3S -filled PMMA before exposure to brine is characterized by two large exothermal peaks at about $320^\circ C$ and $390^\circ C$. The peak at $390^\circ C$ seems to represent the end temperature of degradation of PMMA itself.

In order to determine the thermal stability of the Ca-PMMA complex at 200° , 300° , and $350^\circ C$, tests were performed using a DuPont TGA operated in the isothermal mode. The results, given in Figure 13, indicate good thermal stability at $300^\circ C$ after an initial rapid loss of weight, probably due to the neutral co-ordinated H_2O molecules. The curve at $350^\circ C$ for the complex indicates a gradual weight loss with time, and probably represents the limit of its thermal stability.

The curves of C_3S -filled PMMA before exposure to brine indicate a good thermal stability at $200^\circ C$, however, at 300° and $350^\circ C$ there is a rapid degradation of PMMA with time.

From the results of the thermal behavior tests described above it appears that the thermal stability of the Ca-PMMA complex produced by ionic-bonding between the Ca^{2+} cations and the polyanions in a hot aqueous media is far better than that of C_3S -filled PMMA before exposure.

Figure 12. TGA and DTA thermograms of C_3S -filled PMMA before and after exposure for 10 days to 25% brine at 240°C.

The physical properties of the Ca-PMMA complex were investigated from the results of compressive strength tests of polymer mortar prepared by the addition of 70 wt% silica sand to 12 wt% MMA monomer containing 18 wt% C₃S. Silica flour was also evaluated as a filler and the results compared to those from C₃S. The results given in Table 2, indicate that the strength of Ca-PMMA complex polymer mortar formed during the brine exposure is 54.2 MPa. However, the silica flour-filled PMMA polymer mortar specimens failed in the test as a result of the large expansion produced by the thermal decomposition of the polymer.

The strength reduction of PMMA polymer mortar containing 18% C₃S after 10 days in brine and in a dry oven at 240°C was ~ 56% and ~ 84%, respectively. It appears from these results that the Ca-PMMA complex formed by the hydrothermal conditions has a greater effect on the thermal stability of PMMA polymer mortar than the effect of only the interaction which occurs between the C₃S and the CH₂ group. Also, the hydration products of C₃S which are formed in the hydrothermal environment contribute significantly to the improved compressive strength of samples after exposure to brine.⁹ Furthermore, the data suggest that the addition of only 18% C₃S to polymer mortar makes it possible to significantly improve the thermal stability to temperatures near 240°C.

2.2 Inorganic Cements

Research on high temperature inorganic cements has been completed at one institution and is progress at five others. Short descriptions taken from the most recent report for each program are given below. The full reports are included in the Appendix.

Figure 13. Isothermal degradation of the MMA-C₃S system before and after autoclave exposure.

Table 2

Compressive Strength of PMMA Polymer Mortar Containing C₃S or Silica Flour

Composition ^a	Compressive strength, ^b psi (MPa)		
	Before exposure	After exposure to hot air at 240°C for 10 days	After exposure to brine at 240°C for 10 days
12% P - 70% S - 18% SiO ₂	11,480 (80.4)	371 (2.6)	--c
12% P - 70% S - 18% C ₃ S	17,530 (122.7)	2,850 (20.0)	7,735 (54.2)

a - P = MMA; S = 50 wt% #16 sand (size, 1.19 mm) - 25 wt% #30 sand (size, 0.595 mm) - 25 wt% #100 sand (size, 0.149 mm); SiO₂ = silica flour; C₃S = tricalcium silicate.

b - Values are averages for two 2.2-cm-diam. x 4.4-cm-long cylinder specimens.

c - Failed (large expansion) and removed from test.

Colorado School of Mines

G.L. Kalousek, Principal Investigator

Starting date, April 1977

Completion date, January 31, 1979

The program has been completed and the final report written.¹⁰ Publication in July 1979 is anticipated. The summary and conclusions for the report are given below.

In the present research, no insurmountable difficulties were encountered with selected normal-weight portland cement-silica and β C₂S-silica cements. Similar cements in light-weight slurries showed, on the basis of accelerated tests, possible long-term retrogression for two of the three ultimate binders. Aluminous tobermorite indicated long-term stability up to 250°C or higher. Truscottite at normal weight appeared stable through 90 days at 350°C. In a light-weight cement having a binder comparable with that of the normal-weight product, the strength retrogressed to zero in 7 days at 350°C. Xonotlite as a principal binder exhibited strengths ranging from the highest to mediocre, and questions arose regarding this variability. Some limited published information indicated that light-weight xonotlite may undergo strength retrogression upon prolonged exposure to brine. Evidence on the performance of scawtite, as a fourth principal binder as a replacement for xonotlite, is still meager.

Directions for further research are discussed. It is evident that ultimate and positive evaluation of geothermal well cements established as satisfactory candidates in laboratory tests should be done under actual field conditions.

Dowell Division of Dow Chemical

B.E. Simpson, Principal Investigator

Starting date, July 1977

Completion date, July 1980

The Dowell effort is a three-phase program to develop completion systems for geothermal wells. In Phase I which has been completed, 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.

Significant progress was made this quarter in Phase II of the program. Major progress has been made in several areas: (1) DTA, compressive strength, and bonding measurements were performed on candidate cement systems, (2) the dynamic testing program is now underway in both the laboratory and field sites, and (3) the chemical studies program is now progressing at an accelerated pace with the x-ray system fully operational. Also, E.B. Nelson traveled to Aberdeen, Scotland, to confer with Dr. H.F.W. Taylor concerning research methods with cements at high temperatures.

The fifth progress report for this work is given in Appendix 2.

Battelle's Columbus Laboratories

R.S. Kalyoncu, Principal Investigator

Starting date, September 1977

Completion date, August 1979

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 composition; (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.

To date, tasks on thickening time, compressive strength, permeability, and cement-to-metal bond strength measurements have been completed. Corrosion behavior of the metal casing by the cementing materials has been studied using the half-cell potential technique.

Several cementing compositions have been formulated with chemical, physical, and mechanical durabilities to withstand the existing geothermal conditions. Three such formulations have been submitted to NBS for pilot plant evaluations before a decision is made to use them in field applications.

Major efforts are now being devoted to the characterization of the cementing compositions thus far formulated and found promising for geothermal applications. Extensive characterization studies are presently underway using TEM/SEM/EDAX, DTA, light microscopy, and X-ray diffraction techniques. Complete characterization results are expected to be available by the next reporting period. Details for these efforts are given in Appendix 3.

Pennsylvania State University

D.M. Roy, Principal Investigator

Starting date, September 1977

Completion date, September 1979

The research addresses development of new cements for geothermal applications, utilizing commercially-available components as much as possible. The major systems $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ (CMSh) and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (CASH) constitute the basis for the present study, using a Class J oil well cement and two commercial calcium aluminate cements. The properties of these new high-temperature cements must be such that they extend the performance of usual cements in deep oil wells. Long-term stability within the temperature range 200-400°C is of concern. The strength, physical properties, stable phases, and kinetics of the reactions that form stable phases must be determined in order to insure long-term stability and retention of the beneficial properties.

Because it is difficult to determine with certainty the stable phase reaction products of such commercial cements, where the reactions proceed slowly, several other starting materials also have been used. These alternate materials were also used in an attempt to alleviate problems of impurities, such as carbonate, e.g. carbonate ion, and to understand their effect upon the equilibrium relationships. Data obtained to date are summarized in Appendix 4.

University of Rhode Island

T.J. Rockett, Principal Investigator

Starting date, July 1977

Completion date, August 1979

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.

During the report period work was performed in three major areas. The first area involves the solubility of silicate glasses in phosphate solutions. This area is critical to the type of geothermal cements being investigated in this contract because a glass is the major starting material for the cement. It is the interaction of the glass with a phosphate liquid that forms the cement. If the glass is insoluble in the liquid phase, no cement will result. If there is a major interaction between the glass and the liquid a cement may form so rapidly that no set time will be available for emplacement. Understanding the solubility behavior of the glasses is basic to the selection of a geothermal completion cement.

The second group of experiments is equally important to cement design and involves the equilibrium phase relations between aluminum oxide, calcium oxide and phosphate solutions. The glasses release cementing constituents to the phosphate liquid. Just which constituents should be added to the glasses is determined by these equilibrium studies. The ratio of calcium oxide to aluminum oxide which will react

with various phosphate solutions to yield stable compounds (and therefore could form a stable cement) is the resulting data obtained from the equilibrium studies.

The third phase of the work involves the testing of cements which have been designed using the data from the first two sections. The glass composition which is receiving the major attention at this time is 7% Na₂O:24% CaO:24% Al₂O₃:45% SiO₂. Preliminary tests have shown that this material sets in several hours and appears to have some high temperature stability. Quantities sufficient for further testing are being prepared and longer term tests are being initiated.

The seventh progress report for the project is given in Appendix 5.

Southwest Research Institute

D.K. Curtice, Principal Investigator

Starting date, October 1977

Completion date, October 1979

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 January-March 1979, studies to optimize formulations which will be pumpable at 315°C or higher and set with good compressive and bond strengths have continued. Consistometric tests have indicated that several recipes will give as long as three hours pumping time at 316°C. Systems containing aluminum oxide or zirconium oxide were selected for study at temperatures up to 400°C. These results are summarized in Appendix 6.

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 are in progress at NBS. This work will serve to establish priorities for evaluation in down-hole testing facilities.

NBS has prepared a document giving preliminary recommendations for standardized tests for the evaluation of geothermal cementing materials. The recommended practices, given in Appendix 7, will be reviewed at the June 19, 1979 API Task Group Meeting.

Task 4. Placement Technology

To date pumpability requirements have been met by cements developed at the Colorado School of Mines, Battelle Columbus and Southwest Research Institute and Dowell.

Task 7. Administrative

During the current report period three "Project Status Reports" were submitted to DGE by each of the participating organizations. A draft copy of Quarterly Progress Report No. 11¹¹ was prepared and circulated for review.

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Appendix 1

MINUTES OF MEETING OF API TASK GROUP ON CEMENTS FOR GEOTHERMAL WELLS

Wednesday, January 24 and Thursday, January 25, 1979
Astro Village Hotel - Houston, Texas
Chairman: J.P. Gallus

The chairman opened the meeting at 1:30 PM, January 24, 1979 and welcomed those present. The attendance list is attached.

The research and programs being conducted under the auspices of the Department of Energy (DOE) were reviewed and discussed. The structure and tentative scheduling of the program received particular attention. The development phase of the program which consists of six University and Research Institute contracts is to be completed by October 1, 1979. At that time the results of this work are to be reviewed by the Task Group and recommendations made regarding additional testing of prospective geothermal cements by the National Bureau of Standards (NBS) in Phase 2 of the program.

Materials supplied to NBS from industry and commercial firms will also be evaluated under this phase of the program.

Discussion was held regarding test procedures and methods to be used by NBS. General agreement was reached and detailed procedures are to be established by task group agreement in the near future. The group also discussed whether or not final testing of the most promising cement(s) so determined should be accomplished by a "pump-down cement field test" in an actual geothermal well.

Messrs. F.J. Shell and J.P. Gallus agreed to investigate whether a suitable well for such a test may be available and what the cost of the field test would be. This information will be used by DOE in determining the need for the effort and the level of funding required.

The materials to be tested in the field tests are to be reviewed and recommended by the task group.

The next meeting of the task group will be held in conjunction with the API Standardization Committee meeting in San Diego in June 1979.

TASK GROUP ON CEMENTS FOR GEOTHERMAL WELLS
ATTENDANCE LIST

A meeting of the Task Group on Cements for Geothermal Wells was held on Wednesday, January 24 and Thursday, January 25, 1979 at the Astro Village Hotel, Houston, Texas with Chairman J.P. Gallus presiding.

The following attended:

Curtice, David	Southwest Research Institute	San Antonio, TX
Eilers, L.H.	Dowell	Tulsa, OK
Fuller, Edwin R., Jr.	National Bureau of Standards	Washington, DC
Gallus, J.P.	Union Oil Company of California	Brea, CA
Johnson, Carl E., Jr.	Chevron Oil Field Research Corp.	LaHabra, CA
Kalousek, G.L.	Colorado School of Mines	Lakewood, CO
Kalyoncu, Rustu S.	Battelle Columbus Lab.	Columbus, OH
Kukacka, L.E.	Brookhaven National Laboratory	Upton, NY
Krause, Ralph	National Bureau of Standards	Washington, DC
Meador, Glen	Lone Star Lafarge Inc.	Houston, TX
Mueller, Barbara Jo	U.S. Dept. of Energy	Argonne, IL
Moran, Larry	Dowell	Tulsa, OK
Nelson, Steve	BJ-Hughes Inc.	Arlington, TX
Owens, Byron	BJ-Hughes Inc.	Houston, TX
Pettitt, Roland A.	Los Alamos Scientific Laboratory	Los Alamos, NM
Rockett, Tom	University of Rhode Island	Kingston, RI
Roy, Della M.	MRL, The Pennsylvania State Univ.	University Park, PA
Shell, F.J.	Phillips Petroleum Co.	Bartlesville, OK
Simpson, Ben	Dowell	Tulsa, OK
Stewart, Bruce	Shell Research	THE NETHERLANDS
Sugama, T.	Brookhaven National Laboratory	Upton, NY
Watters, Larry	Halliburton Services	Duncan, OK

DOWELL DIVISION OF DOW CHEMICAL U.S.A.

COO/4190-6

DEVELOPMENT OF GEOTHERMAL WELL COMPLETION SYSTEMS

Phase II: Progress Report No. 5
January - March, 1979

Contributors:

L. H. Eilers	E. B. Nelson
L. K. Moran	L. B. Spangle
B. E. Simpson	

work performed for the
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EXECUTIVE SUMMARY

Significant progress was made this quarter in Phase II of Dowell's geothermal research. Major progress has been made in several areas: (1) DTA, compressive strength, and bonding measurement were performed on candidate cement systems, (2) the dynamic testing program is now underway in both the laboratory and field sites, and (3) the chemical studies program is now progressing at an accelerated pace with the x-ray system fully operational. Also, E. B. Nelson traveled to Aberdeen, Scotland, to confer with Dr. H. F. W. Taylor concerning research methods with cements at high temperatures.

SCREENING PROGRAM

Shear bond tests conducted last quarter were photographed in order to show the residual cement on the pipe cylinders. The photographs were to be included in the last quarterly report, but one of them was inadvertently left out. These pictures have been included in this report as Figures 1 and 2, and should be viewed along with data tables found in the previous report, COO/4190-5.

The results of x-ray analyses of candidate cement systems cured for 28 days at 400°F (217°C) are found in Table 2. Compositions of these systems are found in Table 1. Corresponding compressive strength data is found in the previous quarterly report, Table 1. Some promising results have been noted with System 33, a Class B cement with 35% sand. At 227°C, the compressive strength was low; however, at 316°C the strength was much higher. X-ray diffraction data shows that scawtite is present at 227°C, but is essentially absent at 316°C.

Systems 14 and 15 contained a great deal of scawtite at 316°C and were of low compressive strength. At 227°C System 14 contained a moderate amount of scawtite with a strength of 575 psi (4025 kPa); however, scawtite was not present in System 15, and the compressive strength was 1650 psi (11550 kPa). Another Class B system, 38, contained a moderate amount of scawtite at 227°C with a low compressive strength of 2800 psi, at 316°C, the strength was an excellent 2800 psi and scawtite was absent.

Based on the data presented so far, one would tend to conclude that the presence of scawtite in cement is severely detrimental to compressive strength; however, conflicting data as to scawtite's effect on strength exists. For example, consider Systems 25 and 26. System 25 is a slag cement composition with 35% silica flour and 10% $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$. System 26 is much different, a (1:1) lime:silica mix. Both systems contained major amounts of scawtite, yet were not adversely affected in terms of strength. Such conflicts have occurred fairly often in this research, and evidence is mounting to suggest that one cannot simply label a cement phase as a "high" or "low" strength material.

This subject will be addressed in the chemical studies portion of the report.

Differential Thermal Analysis (DTA) was performed on 38 systems, and reproductions of the actual thermograms are found in Figure 3, which is comprised of eight pages. The systems were originally cured for 28 days at 204°C, the temperature limit of the curing cell, and the minimum temperature at which hydrates should be detected by DTA. If, however, hydrates are found below 204°C, it can be assumed that the test samples were not completely hydrated during the 28 day curing period, or some of the hydrated products converted to low temperature hydrates. Such hydrates are detected as negative peaks, or endotherms, on the thermograms. Systems 12, 17, 18, 25, 26, 34, and 37 show this behavior.

Expansion tests will be conducted next quarter. A prototype device has been designed that can measure expansion of a cement system while under high temperature and pressure. Details concerning the design and performance of this device will be presented in the next quarterly report.

DYNAMIC EVALUATION PROGRAM

The Dynamic Brine Exposure Testing Apparatus (D-BETA) underwent preliminary testing this quarter in an effort to debug the system prior to running actual test samples. There were several start-up difficulties, but most have been corrected. One remaining problem is a gradual buildup of calcium carbonate and silica scale in the one meter of tubing between the ends of the sample containers and the exit from the furnace (see Report No. COO/4190-4). The scale deposition has been reduced somewhat by increasing the rate of brine flow through the system.

Based on preliminary results, the rate at which cement coupons undergo change in the D-BETA lies between that of the static tests and the dynamic exposures at East Mesa, California. Such behavior is logical because the brine circulation rate in the D-BETA is 0.05 to 0.15 liter/minute while the rate at East Mesa is 6.0 liters/minute or more. Not surprisingly, sample erosion at East Mesa was considerable due to the rapid fluid movement. Erosion was not evident in the D-BETA samples. Also, lightweight cements deteriorated more than normal compositions in both dynamic exposure systems. Table 3 lists the initial composition of the dynamically exposed systems, and Table 4 is a compilation of permeability and compressive strength data for these cements when exposed to the D-BETA and East Mesa systems.

The major difference between static and dynamic geothermal testing of the cement coupons lies in the nature of the crystalline phases that occur. Under static conditions, some common type of calcium silicate hydrate such as xonotlite, truscottite, tobermorite, or scawtite usually forms. Dynamic exposure with

brines containing carbon dioxide as bicarbonate results in the formation of calcite or aragonite with considerable unreacted residual quartz. There is also a considerable amount of silicate material in these samples, but it is undetectable by x-ray diffraction due to its poorly crystalline or even completely amorphous state. Table 5 lists the detectable compositions of these geothermal cements.

Lack of crystallinity in dynamically exposed cements does not appear to have a significant effect on strength and permeability. Systems that were strong upon static exposure were able to maintain strength when dynamically treated. Conversely, cements that were weak when statically tested tended to be weaker still after dynamic exposure. Two possible explanations for this behavior are apparent. (1) A tightly packed and strong crystal structure may maintain itself regardless of whether the composition is a calcium silicate hydrate or calcite. (2) A non-crystalline binding compound exists between crystals that lends adherence and strength to the cement. The second explanation appears to be more plausible in light of the apparent non-crystallinity of samples dynamically exposed to a geothermal environment. Examination of these samples by scanning electron microscopy is indicated.

CHEMICAL STUDIES

The chemical studies portion of Dowell's geothermal research progressed at an accelerated pace this quarter with the new advanced x-ray diffraction system finally operational. All that remains to be done now is interfacing the system with a computer, targeted for early April. When automation is complete, samples will be processed much more quickly and accurately than the manual approach currently being used. The capabilities of this system will be described in more detail next quarter.

Highlighting this quarter's chemical studies work was E. B. Nelson's journey to the University of Aberdeen, Scotland, for consultation with a recognized leader in the field of cement chemistry and calcium silicate mineralogy, Dr. H. F. W. Taylor. The principal purpose of the trip was to observe Taylor's research methods pertaining to cements at elevated temperatures and pressures, and to discuss some of our results in terms of proper interpretation. Despite his busy schedule, Professor Taylor was very generous with his time and gave us a great deal more insight in dealing with materials as complex and, at times, unpredictable as the calcium silicate hydrates.

Rather than using Portland cement with associated bulk materials, Taylor does most of his research with materials such as pure lime, silica, aluminum oxide, etc., to minimize spurious interferences and allow close scrutiny of a particular aspect of calcium silicate chemistry. Basic research at Dowell is done in much the same way; however, ultimately the chemical knowledge gained must be transferred to the impure cements and fly ashes for economic reasons.

Taylor's basic sample preparation procedure involves thorough mixing of pure raw materials. A one gram sample of the mixture is placed in a silver tube and autoclaved at a specific temperature for periods usually ranging from 4 to 21 days. The curing pressure is usually the saturated steam pressure for the temperature of interest; however, higher pressures may be applied if necessary. After curing, the product is immediately washed in acetone and dried in air.

X-ray diffraction analysis is performed using a Hägg Guinier camera. The Guinier camera has a geometry such that a strip of film records intensity data linearly by 2θ , much like a diffractometer scan. A densitometer is used to convert the developed film to an intensity vs. d-spacing format. The advantage of the Guinier method lies in its ability to generate extremely detailed data of a high signal to noise ratio with samples of less than 0.01g. This is a major departure from Dowell's use of the powder diffractometer. Fine as Guinier data may be, obtaining a 0.01 g sample of a Portland cement specimen that is representative of the whole would be most difficult and definitely impractical. For pure lime-silica work, though, the Guinier technique is incomparable.

Taylor's laboratory obtains extraordinarily fine results with the Guinier due to a special recording densitometer that was developed by another U. of Aberdeen faculty member, Mr. Brian Cooksley. The film strip containing the x-ray pattern is inserted around a small turntable which rotates at 500 RPM. A light beam from a tungsten source passes through the film and a photoelectric cell on the other side detects the light transmitted. A small computer divides the turntable circumference into 100,000 parts, and each time the turntable rotates, the computer advances by one part and digitizes the transmitted intensity. A pictorial representation of the pattern can be seen either on a CRT on a chart recorder. The quality of the resulting x-ray pattern is extraordinarily detailed and the signal to noise ratio is very high.

After x-ray analysis the hydrated product is analyzed for average C/S ratio by atomic absorption. A La standard is necessary during the analysis to mask the Si interference with Ca absorption. These analyses have shown that SiO_2 will enter the vapor phase of the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system at temperatures above 275°C . The implication here is that low strength - silica deficient calcium silicate hydrates are favored at geothermal temperatures. Similar data has been found by L. H. Eilers and E. B. Nelson and was recently published (SPE 7875). Their data showed that silica-deficient calcium silicates will form in a geothermal environment unless the added silica is very fine. The explanation for this behavior was that a decrease in the rate of solution of silica is responsible. Taylor's discovery may show that SiO_2 vaporization is another factor to consider.

For the last several months we have been sending geothermal cement samples to Taylor for analysis in hopes of identifying

the phase responsible for the unidentified 3.50Å line that seemed to be related to strength. This subject was discussed in the previous quarterly report. At first we and Taylor thought the phase was simply anhydrite, but rejected that notion because none of the supplementary peaks for that mineral were present. Many other possible explanations, including a new calcium silicate hydrate, were postulated, but none proved conclusive.

During the Aberdeen visit, Taylor and Nelson worked further on the problem and came to the conclusion that the peak is in fact due to anhydrite as we had originally suspected. The intensity of the principal of anhydrite peak at 3.493Å is evidently highly affected by preferred orientation. In general, the peak has been weak upon Guinier analysis and strong, though not reproducible in intensity, if the diffractometer is used. When the samples were heated to 350°C, the intensity of the peak was unaffected, but extraction with boiling water caused it to disappear. When the aqueous extract was evaporated to dryness in a steam bath, the residue contained $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ or a closely related phase. On heating the residue to 350°C the lines attributed to $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ disappeared and the anhydrite lines appeared. Elemental analysis by electron microprobe showed Ca and S also. However, Si was present in some particles whose identity has not been determined as yet.

In our geothermal work and in other cement related research, the tendency has generally been to label a particular phase as "good" or "bad" in terms of strength and permeability. Evidence has been mounting which suggests that such a simplistic approach does not suffice. A phase must be also evaluated in terms of the context of its usage, degree of crystallinity, and the matrix in which it appears.

In this quarterly alone three examples of this are evident. First, the conflicting data in samples containing the phase scawtite shows that more detailed observation will be necessary to fully understand this system. The differences in crystallinity between statically and dynamically exposed cements and their related strength demand a more thorough analytical approach. Finally, the 3.50Å line and its reported relationship with strength will require more research. The degree of preferred orientation may relate to the crystallinity of the sample and its strength. To examine cements more thoroughly, scanning electron microscopy is definitely indicated. The factors which determine strength and permeability of cement seem to be much more subtle than simply which phase has formed. In the future we plan to do SEM work in hopes of better understanding these parameters.

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ADDITIVE CODES

<u>Code</u>	<u>Material</u>
ALOH	Aluminum hydroxide, Al(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
GIL	Gilsonite
MgO	Magnesium oxide

Table 1

Compositions of Candidate Geothermal Cement Systems

* Percent by weight of water		Additives (% BWOC)						Retarder	
System #	Cement Type	Code	%	Code	%	Code	%	% Water	Code %
1	Permanente "G"	Sand	35					54	1 1.0
2	Permanente "G"	SF	35					54	1 1.0
3	Permanente "G"	SF	35	FA-N	79			52	1 1.0
4	Permanente "G"	SF	35	PERL	8.5	BENT	2.0	116	1 1.0
5	Permanente "G"	SF	35	NaCl	37*			54	1 1.0
6	Permanente "G"	SF	35	NaCl	10*			54	1 1.0
7	Permanente "G"	SF	35	KCl	37*			54	1 1.0
8	Permanente "G"	SF	35	KCl	10*			54	1 1.0
9	Permanente "G"	SF	35	DE	8.9			91	1 1.0
10	Permanente "G"	SF	35	COAL	27			63	1 1.0
11	Permanente "G"	SF	35	GIL	27			63	1 1.0
12	Unadeep "J"							44	1 0.4
13	Unadeep "J"	FA-N	79					75	1 0.4
14	Unadeep "J"	PERL	8.5	BENT	2.0			106	1 0.4
15	Unadeep "J"	BENT	4.0					65	1 0.4
16	Unadeep "J"	BENT	8.0					86	1 0.4
17	Unadeep "J"	NaCl	37*					44	1 0.2
18	Unadeep "J"	KCl	10*					44	1 0.2
19	Unadeep "J"	SSS	2					90	1 0.2
20	Fondu							50	1/2 1.5/1.5
21	Fondu	FA-N	85					81	1/2 1.5/1.5
22	Slag Cement	SF	35					56	1 1.25
23	Slag Cement	SF	35	FA-N	79			93	1 1.25
24	Slag Cement	SF	35	SSS	1.5			122	1 1.25
25	Slag Cement	SF	35	PP	10			74	1 1.25
26	Lime:Silica (1:1)							96	1 0.7
27	Lime:Silica (1:1)	ALOH	7.0					96	1 1.0
28	Lime:Silica (1:1)	PERL	8.5	BENT	2.0			110	1 0.7
29	Lime:Silica (1:1)	FA-N	79					130	1 1.0
30	Lime:Silica (1:1)	FA-N	79					130	1 1.0
31	Lime:Silica (1:0.4)							142	1 0.7
32	Millwhite Pozz:Lime (1:0.42)							142	1 0.7
33	"B"	SAND	35					56	1 1.2
34	"B"	SF	35					56	1 1.5
35	"B"	SF	35	PERL	8.5	BENT	2.0	118	1 0.6
36	"B"	SF	35	KCl	37*			56	1 1.0
37	"B"	SF	35	NaCl	37*			56	1 1.0
38	"B"	SF	35	FA-L	79			120	1 1.0

Table 2

X-Ray Analysis of Laboratory Screening Program
Cured 28 Days at 204°C Under Water

SYSTEM #	MAJOR	MINOR	LOW
1.	Xonotlite	--	--
2.	--	Xonotlite	--
3.	--	Tobermorite (11.3A)	Quartz
4.	Xonotlite	--	Tobermorite
5.	--	Kilchoanite, Dicalcium Silicate	Xonotlite
6.	Xonotlite	--	--
7.	Xonotlite	--	Rustunite
8.	Xonotlite	--	--
9.	Xonotlite	--	--
10.	Xonotlite	--	--
11.	Xonotlite	--	--
12.	--	Scawtite	--
13.	--	Tobermorite (11.3A)	Quartz, Calcite
14.	--	Tobermorite (11.3A), Scawtite	Quartz
15.	--	Tobermorite (11.3A)	Quartz, Calcite
16.	--	Tobermorite (11.3A), Scawtite	Quartz
17.	--	--	Tobermorite (11.3A), Quartz, Scawtite, Xonotlite
18.	Tobermorite (11.3A)	--	Quartz, Scawtite
19.	Xonotlite	--	--
20.	Xonotlite	--	--
21.	Xonotlite	--	Tobermorite (11.3A)
22.	--	Tobermorite (11.3A), Xonotlite	--
23.	Xonotlite	--	--
24.	--	Tobermorite (11.3A)	Quartz
25.	Scawtite	--	Tobermorite (11.3A)
26.	Scawtite	--	Tobermorite (11.3A), Quartz
33.	--	Scawtite	Tobermorite (11.3A)
34.	--	--	--
35.	--	--	Quartz
36.	--	Xonotlite	Tobermorite (11.3A), Scawtite
37.	--	Tobermorite (11.3A), Quartz	--
38.	--	Tobermorite (11.3A), Scawtite	--

Table 3

(A) Dynamic Brine Exposure Systems

Cement		Additives (% BWOC Unless Otherwise Indicated)								%H ₂ O
		Additive	%	Additive	%	Additive	%	Additive	%	
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.	Lime-Silica (1:1)	SR	0.7	---	-	----	--	----	-	96
19.	Lime-Silica (1:1)	SR	1	Al ₂ O ₃	7	----	--	----	-	96
20.	Lime-Silica (1:1)	SR	0.7	PERL	8.5	BENT	2	----	-	110
21.	Lime-Silica (1:1)	SR	1	FA/N	79	----	--	----	-	130
22.	Lime:FA/N (0.4:1)	SR	0.7	----	-	----	--	----	-	100
23.	Lime:Pozz (0.4:1)	SR	0.7	----	-	----	--	----	-	142
24.	Ideal B	SAND	35	SR	1.0	----	--	----	-	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
33.	Kaiser G	SF	100	SR	0.8	----	--	----	-	72

* By weight of ash + cement

Table 4 (B)

Dynamic Brine Testing
See Previous Table for Composition of Each System

System No.	D-Beta Results - 160°C				East Mesa Results - 152°C				Diameter Reduction 3 month
	Water Perm-Mds		Comp. Strength PSI		Water Perm-Mds		Comp. Strength-PSI		
	2 week	1 month	2 week	1 month	1 month	3 month	1 month	3 month	
1	0.011	0.032	4000	5300	0.03	0.002	2825	500	12%
2	0.002	0.009	8400	10375	0.01	0.001	1500	900	12%
3	0.004	0.035	4825	4225	0.02	0.01	2250	1400	12%
4	0.072	0.098	1600	1100	0.06	0.01	875	1400	12%
5	0.003	0.063	5500	4250	0.05	0.01	1250	1200	12%
6	0.002	--	7200	--	0.01	--	1100	--	---
7	0.013	--	8025	--	0.17	--	2800	--	---
8	0.053	0.044	3775	2600	0.06	0.04	2800	1475	25%
9	0.005	--	4500	--	0.08	0.16	1725	1825	12%
10	0.049	0.041	2700	3750	0.18	0.41	2700	3750	12%
11	0.006	0.078	3575	2950	0.10	0.35	1825	775	19%
12	0.76	--	650	--	0.19	--	475	--	---
13	0.141	--	2125	--	0.94	--	1425	--	---
14	0.149	0.092	1550	2150	0.22	--	1250	--	---
15	0.028	--	2375	--	0.04	--	2700	--	---
16	0.070	--	3250	--	0.03	--	2025	--	---
17	Soft	--	50	--	Soft	--	50	--	---
18	Soft	--	25	--	Soft	--	Soft	--	---
19	0.181	0.195	1525	825	0.43	--	100	--	---
20	Cracked	--	350	--	Soft	--	25	--	---
21	1.27	--	275	--	0.50	--	250	--	---
22	Soft	--	75	--	0.89	--	50	--	---
23	Soft	--	75	--	Soft	--	50	--	---
24	0.018	0.027	2150	2575	0.01	0.01	2500	725	6%
25	0.008	0.012	6400	5900	Cracked	0.006	2025	1250	12%
26	0.110	0.103	1750	1500	0.20	--	700	--	---
27	0.010	--	3850	--	0.04	0.09	1825	875	19%
28	0.002	--	5525	--	0.09	0.002	2825	975	19%
29	0.019	--	6325	--	0.08	0.45	1525	775	19%
30	0.020	0.056	4350	1925	0.04	0.01	3575	1000	12%
31	0.133	0.114	925	1525	0.16	--	775	--	---
32	0.069	--	625	--	0.24	--	425	--	---
33	--	0.034	--	1675	--	0.07	--	675	12%

--Indicates this sample not run

One month East Mesa results previously reported Progress Report #4, Table VIII.
Similar compositions under static conditions reported Progress Report #4, Table I.
Brine compositions reported Progress Report #4, Table VI and Progress Report #2,
Table III.

Table 5

Crystalline Composition of Aged Geothermal Cements

Comparison of cements aged static, on slow dynamic (D-Beta) and rapid dynamic (East Mesa) fluids. Cements listed in Table 3 (A).

No.	<u>1 Day Cure</u>	<u>28 Day Static</u>	<u>14 Day D-Beta</u>	<u>28 Day E. Mesa</u>
		<u>227 & 316°C</u>	<u>160°C</u>	<u>153°C</u>
1.	CSH-Q	Xon-Rus	Q-Cal-C ₂ SH	Cal-CS ₂ H
2.	CSH-Q	Xon-Cal	Q-CSH	Q-Cal
3.	Tob-Q	Tob-Ros	Tob-Q	Cal-Q
8.	CSH-Q	Xon-Cal	Q-Cal	Cal-Q
10.	Q-Tab	Q-Cal	Q-Ar	Cal-Q
12.	Tob-Q	Scaw-Trus	Q-Tob	Cal-Tob
14.	Tob-Q-Cal	Q-Xon	Cal-Q	Cal-Q
17.	Q-Cal	Scaw-Trus	Cal-Q	Cal-Q
18.	Tob-Q-Cal	Xon-Cal-Q	Cal-Q	Cal-Q
19.	Tob-Q	Xon	Cal-Tob	Cal-Q
21.	Q-Tob	Trus-Xon	Cal-Q	Q-Cal
25.	Q-CSH	Xon-Cal	Xon-Q	Cal-Q
26.	Tob-Q	Xon-Cal	Cal-Tob	Cal-Q
32.	Tob-Q-Cal	Tob-Cal	Cal-Xon-Q	Cal-Q

Abbreviations:

Ar - Aragonite (CaCO₃)
 CSH - Calcium Silicate Hydrate
 C₂SH - Dicalcium Silicate Hydrate
 CS₂H - Calcium Hydrate Disilicate
 Cal - Calcite (CaCO₃)
 Q - Quartz
 Ros - Rosenhahnite
 Rus - Rustumite
 Scaw - Scawtite
 Tob - Tobermorite
 Trus - Truscotite
 Xon - Xonotlite

Figure 1. Residual Cement After Shear Bond Testing
(See data tables in Report C00/4190-5, page 10,
Table I).

Figure 2. Residual Cement After Shear Bond Testing
(See data tables in Report C00-4190-5, page 10,
Table I).

Figure 3. Differential thermal analysis of cement cured 28 days at 400°F. All systems retarded for placement time. Deltatherm D2000, Heat Rate = 10°C/Min., ΔT Sensitivity 1°C/25.4 mm, 2-22-79 (1/2 scale simulated thermograms). (See Table I for detailed descriptions)

Figure 3 (cont'd)

Figure 3 (cont'd)

Figure 3 (cont'd)

Appendix 3

QUARTERLY TECHNICAL PROGRESS REPORT
December-February, 1979

on

HIGH TEMPERATURE CEMENTING MATERIALS
FOR COMPLETION OF GEOTHERMAL WELLS

to

BROOKHAVEN NATIONAL LABORATORY

April 11, 1979

by

Rustu S. Kalyoncu and M. Jack Snyder

Under Contract No. 420825-S

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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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

QUARTERLY TECHNICAL PROGRESS REPORT
December-February, 1979

on

HIGH TEMPERATURE CEMENTING MATERIALS
FOR COMPLETION OF GEOTHERMAL WELLS

to

BROOKHAVEN NATIONAL LABORATORY

INTRODUCTION AND SUMMARY

We are in the final phase of a two year program designed to develop high temperature cementing materials to be used in the completion of geothermal wells. The research program was designed to develop cementing materials which would withstand the chemical, physical, and mechanical conditions encountered in geothermal wells.

Tasks on thickening time, compressive strength, permeability, and cement-to-metal bond strength measurements have been completed. Corrosion behavior of the metal casing by the cementing materials has been studied using the half-cell potential technique.

Several cementing compositions have been formulated with chemical, physical, and mechanical durabilities to withstand the existing geothermal conditions. Three such formulations have been submitted to NBS for pilot plant evaluations before a decision is made to use them in field applications.

Major efforts are now being devoted to the characterization of the cementing compositions thus far formulated and found promising for geothermal applications. Extensive characterization studies are presently underway using TEM/SEM/EDAX, DTA, light microscopy, and X-ray diffraction techniques. Complete characterization results are expected to be available by the next reporting period.

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 uses and builds 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 was 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 were 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 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 were subjected to a more detailed performance, evaluation tests relating to their use in the lining of geothermal wells. Specifically, considerations were 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
- Task No. 7 - Detailed characterization of cementing compositions of interest.

For this period the characterization work was initiated on five compositions showing promise for geothermal well completion applications. Samples of three of the compositions have been sent to Dr. Ed Fuller at National Bureau of Standards for further evaluation tests.

Task No. 1 - Thickening Time Measurement

All the thickening times were measured using the API high temperature and pressure consistometer under approximate conditions of 400 F temperature and 3000 psi pressure. Typical thickening times obtained were in the range of 100 to 150 minutes with several compositions exhibiting thickening times of 200 to 250 minutes.

Task No. 2 - Compressive Strength of Cements

Compressive strength measurements on a large number of formulations with class J oil well cement, pozzolan, silica flour, and blast furnace slag combinations were carried out at room temperature and under autoclave conditions. The data and analysis were given in the previous Quarterly Technical Progress Reports. The compressive strength data on one of the current compositions that were submitted to NBS for further evaluations agree well with the findings of NBS. A total of three cementing compositions have been submitted to NBS for pilot plant evaluations.

Task No. 3 - Permeability Measurements

Liquid and gas permeabilities of a dozen cementing compositions have been measured. Most of the liquid permeability values are within the range of 0.1 md. Numerical values of permeabilities were reported in the previous reports.

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

Bond strength measurements have been made on all cementing compositions developed. In all cases more than adequate cement-to-metal bond strengths have been observed. These measurements were again conducted, as in the case of compressive strength measurements, both at room temperature and under autoclave conditions.

Task No. 5 - Corrosion Behavior of Steel Casing by the Cementing Materials

Electrochemistry of corrosion process of the metal casing by the cements was studied using the half-cell potential measurement technique. As mentioned in the previous report, this method determined primarily whether the corrosion promoting electrochemical conditions exist in the cement-metal systems. It does not measure the corrosion rates per se, and does not measure any physical damage that may be inflicted to the cement structure as a result of corrosion. The method, however, has proven to be a very useful non-destructive technique in indicating corrosion activity in the cement-steel structures.

As pointed out in the previous quarterly progress report, the corrosive effect of most of the cementing compositions studied in the metal casing seem to be minimum. This does not seem to pose a limitation to use of these cementing compositions in the completion of geothermal wells.

Task No. 6 - Compatibility of Cementing Materials with Drilling Muds

Montmorillonitic clay has been used in the amounts of 1 to 7 percent by height of solids in a number of cementing materials to simulate bentonite base drilling muds. No adverse effects of montmorillonite on physical and mechanical properties of the cements have been observed.

Efforts in obtaining industrial drilling muds that are being used in drilling operations have proven fruitless.

It is anticipated that due to improvement in drilling operations and annulus washing procedures prior to cementing possible incompatibility of the cementing compositions with the drilling muds will not present a serious problem.

Task No. 7 - Characterization Studies

Characterization activities on five cementing compositions with possible application to geothermal wells are underway. Characterization procedures include X-ray diffraction, DTA/DSC, light microscopy, and

scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray analysis (EDS).

The diffraction pattern was taken using a Phillips verticle goiniometer with a curved graphite monochromator and scintillation detector. A Cu X-ray tube operated at 35 kv and 20 ma produced the incident X-ray beam. A 1 divergence slit and 1/2 receiving slit were used with a detector voltage of 900 V. The counting system time constant was 1 sec. and the scan rate was 1/min. A Perkin-Elmer Model DSC-2 differential scanning calorimeter is being employed in the thermal analysis of the samples.

In recent years Differential Scanning Calorimetry (DSC) has become the dominant technique in the field devoted to the measurement and characterization of the thermal properties of materials.

This instrument provides automatic electrical compensation for thermal energy changes in the sample, so that the sample is held in close temperature control even during a transition or reaction, and the required compensating electrical power is read out as ordinate in millicalories per second. This new capability means that peak areas are recorded directly in energy units. This represents a revolutionary development in the field of thermal analysis.

Scanning-transmission electron microscopy coupled with energy dispersive X-ray analysis is also being used for further characterization of the cementing formulations. Particle shapes, morphology, and identification of various reaction products are hoped to be accomplished in this study. Elemental compositional comparisons are being made between particulate types of the cementing compositions and single hydrates prepared hydrothermally. In this effort it is essential to prepare specimens for analysis with well dispersed powders, where a single particle can be focused on, in order to avoid obtained X-ray spectra from the adjacent particles or from the agglomerates containing several different compounds. Consequently, several techniques of specimen preparation have been explored to achieve this end. It has not been possible to obtain the desired degree of particle dispersion merely by drying a suspension. Attempts to make dispersions on plastic sheet, coating with carbon film and dissolving away the plastic sheet by the Jaffe method also was not successful. However, dispersing the five particles in ethyl alcohol by ultrasonic treatment to break agglomerates

followed by filtration of various size aliquots to deposit the particulates on millipore filters resulted in satisfactorily dispersed specimens for our purposes.

The analysis will be made by electron microscopy coupled with energy dispersive X-ray analysis (EDS) to identify various compounds by determining the elemental ratios (e.g., Si/Ca) in single particles. The instrument is a scanning-transmission electron microscope (STEM) which can image structures in three different ways. It can be used as a conventional transmission electron microscope (CTEM), with a stationary beam and electromagnetic lenses (to image at high magnification and resolution) to study specimens which are sufficiently thin to be penetrated by the electron beam. It can also image surface structure in the scanning mode where secondary electrons emitted from the surface of the specimen are detected; or it can image internal structure in the scanning-transmission mode where images could be obtained from thicker specimens than in the CTEM mode because there is no deterioration of the image due to chromatic aberration during scanning. The small beam size ($\sim 50 \text{ \AA}$) also makes it possible to select a structure and excite X-rays from very small regions of a specimen for elemental analysis. This feature is important in meeting the objectives of a single particle analysis which is intended in this study.

The energies of the X-rays generated by the electron beam are detected by a lithium-drifted silicon crystal detector; the elements are identified and quantitative determinations are made by a data processing computer. Data processing includes automatic programs for identification and quantification of the signals from the X-ray detector. Distribution of elements may be mapped and correlated with scanning electron microscope images of specimen structures. Additional computer programs can be written to meet special analytical needs.

X-ray diffraction, and DTA patterns along with some STEM/EDX data have been obtained and preliminary observations have been made. Additional characterization data will be obtained and evaluated before statements of conviction are made about the nature, composition, and mechanistic behavior of these cementing systems.

Appendix 4

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
December 1, 1978 - February 28, 1979

March 15, 1979

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1. INTRODUCTION

The current research addresses development of new cements for geothermal applications, utilizing commercially-available components as much as possible. The major systems $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ (CMSh) and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (CASH) constitute the basis for the present study, using a Class J oil well cement and two commercial calcium aluminate cements. The properties of these new high-temperature cements must be such that they extend the performance of usual cements in deep oil wells (Roy, *et al.*, 1979). Long-term stability within the temperature range 200-400°C is of concern. The strength, physical properties, stable phases, and kinetics of the reactions that form stable phases must be determined in order to insure long-term stability and retention of the beneficial properties.

Because it is difficult to determine with certainty the stable phase reaction products of such commercial cements, where the reactions proceed slowly, several other starting materials also have been used. These alternate materials were also used in an attempt to alleviate problems of impurities, such as carbonate, e.g. carbonate ion, and understand their effect upon the equilibrium relationships. The compositions of (a) cement-based and (b) oxide mixtures are given in Table 1; previous data with a third type of mixture (c) utilizing calcined chrysotile as a starting component have been reported elsewhere (Roy, *et al.*, 1979).

Figure 1 shows an equivalent graphical representation of the mixture compositions (neglecting CO_2 and trace components) as well as some of the hydrous and anhydrous mineral phases within the CMSh system. Mixtures were adjusted to straddle various joins which seemed to hold promise, not only as areas of potentially usable cements but also as having importance in interpreting phase relationships.

2. PREPARATION OF CEMENT

The starting materials used in studies related to development of new hydrothermal cements included $\beta\text{-C}_2\text{S}$, commercial cements, reagent oxides, quartz (Minusil), dehydrated gels, and calcined chrysotile in various

Table 1. Weight percent of starting materials.

Mixture	Type J	CaO	MgO	SiO ₂
MCS-1	75	--	22	3
MCS-5	65	--	19	16
MCS-2	60	--	18	22
MCS-3	57.5	--	17	25.5
MCS-4	55	--	16	29
MCS-11	--	30	22	48
MCS-15	--	26	19	55
MCS-12	--	24	18	58
MCS-13	--	23	17	60
MCS-14	--	22	16	62

combinations. For determining phase stability relationships, mixtures of reagent grade oxides (MgO and CaO) and Minusil (quartz) were used. The experimental procedures were identical for both the oxide and cement mixtures which were cured in noble metal tubes. Here the mixtures were weighed accurately, then mixed into a paste with either deionized water or a saturated NaCl solution with a w/s of 0.45 (neglecting the NaCl in the brine solution). After the pastes were placed in the tubes they were heat sealed using a hydrogen-oxygen flame torch. Eight sets of experiments were carried out at each composition, four with a saturated NaCl solution, and four with deionized water. Each group of four included one prepared with oxides, one cured at 300°C, one at 400°C; and one prepared with cements, one cured at 300°C, one at 400°C. The results of this study comparing the oxide- and cement-based mixtures are presented as a series of tables (Tables 2 through 5).

Other sets of samples were prepared and inserted dry into the noble metal tubes, after which they were crimped closed and cured in the presence of excess water. The conditions of hydrothermal curing included temperatures from 200 to 400°C and pressures of 17.2 to 172 MPa. Results of these experiments were reported previously (Roy, *et al.*, 1979).

Larger cylindrical samples, 50 mm high x 25 mm diameter, were prepared using β -C₂S and 5- μ m Minusil, in addition to reagent oxides [reagent MgO and CaO plus Minusil (SiO₂)] and calcined chrysotile (650°C, 1 hour).

Samples were either inserted into steel tubing (35 mm and 50 mm diameter) or host rocks (either quartzite or limestone) then placed in a 500 ml Barnes inconel (75 x 250 mm) autoclave. The autoclave pressure is built up by the increase in temperature, then, if necessary, pumped to the desired pressure. A few samples were cured for 24 hours at constant humidity of greater than 95 percent before curing in the autoclave. Results for these samples have also been reported previously (September 1978 Quarterly Report).

3. PHASE RELATIONS AND CHARACTERIZATION

Because compositions at or near the diopside composition within the CSMH system showed the highest strength characteristics after hydrothermal curing at 300 and 400°C for 7 to 98 days, these were studied in detail. The compositions of mixtures shown in Figure 1, MCS-1 to 5, and MCS-11 to 15 were designed to straddle the joins of potentially usable cements and also for interpretation of the stable phase relationships, particularly adjacent to the diopside composition.

Deionized Water: 300°C Curing (Table 2) CSMH SYSTEM

Reacted mixtures prepared from Class J cement were found to contain scawtite [$\text{Ca}_7\text{Si}_6\text{O}_{18}(\text{CO}_3) \cdot 2\text{H}_2\text{O}$] in varying amounts. In addition, there appears to be an inverse relationship between the amounts of scawtite and xonotlite. Scawtite increases as xonotlite decreases; this may result from their relatively small compositional difference (except for CO_2 present in scawtite*). Scawtite dominates mixtures 2, 3, and 4; xonotlite dominates mixtures 1 and 5, with the appropriate companion phase playing a relatively minor role. Talc was found in all mixtures, increasing slightly as the mixtures become more silica rich. Chrysotile is a major constituent in mixtures 1 and 5, which have the least silica. Unreacted quartz increases as the mixtures become more silica rich. Unexplainedly, $\beta\text{-C}_2\text{S}$ seems to increase as well.

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

Figure 1. The system CaO-MgO-SiO₂-H₂O and position of starting materials.

Table 2. Comparison of product phases on cement and oxide pastes hydrothermally treated in deionized water at 300°C and 68.9 MPa for 7 days.

Mixture	Class J Cement + Minusil + MgO	Mixture	Oxides
MCS-1	xonotlite tr scawtite tr talc tr chrysotile (?) tr unknown d = 2.374	MCS-11	xonotlite chrysotile diopside tr talc (?) tr unknown d = 2.374
MCS-5	xonotlite scawtite tr talc tr unknown d = 3.009, 3.850	MCS-15	xonotlite diopside chrysotile unknown d = 3.891, 3.842 tr talc (?)
MCS-2	scawtite talc quartz tr xonotlite	MCS-12	diopside talc xonotlite tr chrysotile tr quartz tr truscottite (?) unknown d = 1.993, 1.985, 1.852
MCS-3	scawtite quartz tr xonotlite tr talc tr β -C ₂ S	MCS-13	xonotlite quartz diopside talc truscottite (?) unknown d = 3.978, 3.677, 1.985, 1.850
MCS-4	scawtite quartz talc unknown d = 3.137, θ = 28.45 tr β -C ₂ S (?)	MCS-14	quartz diopside xonotlite talc unknown d = 3.986 scawtite (?) truscottite (?)

In contrast, the corresponding oxide mixtures do not contain scawtite. This is due to the absence of a carbonate impurity in the oxide components. Xonotlite is again a major phase in compositions 11 and 15 (equivalent to cement mixtures 1 and 5) showing a gradual decrease as the mixture becomes more silica rich. Diopside becomes a dominant phase in mixtures 12 to 14 (2-4) as xonotlite becomes minor. Chrysotile decreases and talc in-

creases as the mixtures become silica rich. Unreacted quartz dominates the most silica rich mixture, MCS-14 (4) showing a gradual increase from 11 to 14.

The major differences between the products of runs with oxides vs. those with cement starting materials seem to be that scawtite is absent from the oxide runs, and that diopside rather than xonotlite dominates the oxide runs. The latter observation seems once again to indicate the effect of structural control and kinetics. Either xonotlite (+ chrysotile) or diopside (+ H_2O + ?) is the metastable intermediate phase assemblage. In previous long-term runs with similar mixtures, all three phases are still present after 96-98 days of hydration in mixtures nearest the diopside composition. Due to the fine-grain size and reactivity of the oxides, diopside appears to form preferentially. The presence of carbonated lime in the Class J cement masks the formation of stable phases in the CSMH system. Also, the Class J cement contains β - C_2S which may hydrate and react with silica to form xonotlite and scawtite faster than it is available in solution to combine with the MgO (and SiO_2) to form diopside. The xonotlite or scawtite forms first and then must react with a magnesium-rich phase to form diopside.

Saturated NaCl: 300°C Curing (Table 3) CSMH System

The products of mixtures prepared from Class J cement with a saturated NaCl solution used as the mixing water have a constant amount of NaCl throughout. Scawtite is no longer the dominant silicate phase, but is present at most in trace amounts. Xonotlite is the major phase in lower-silica mixtures, and it and scawtite now both decrease slightly as the silica content increases. Chrysotile is major only in the most silica-poor mixture (MCS-1). It decreases and disappears with increasing silica content, gradually replaced by increasing talc. Diopside is relatively minor but nearly constant throughout. Unreacted quartz once again increases in the silica-rich mixtures.

In products from runs with either type of starting material, the contents of talc and chrysotile phases vary with SiO_2 content as expected. Talc increases and chrysotile decreases with increasing silica content. NaCl is fairly constant throughout, which suggests that it does not react extensively. Xonotlite and diopside both decrease with increasing silica content, as

Table 3. Comparison of product phases in cement and oxide pastes hydrothermally treated in saturated brine at 300°C and 68.9 MPa for 7 days.

Mixture	Class J Cement + Minusil + MgO	Mixture	Oxides
MCS-1	NaCl scawtite chrysotile quartz diopside xonotlite	MCS-11	NaCl xonotlite chrysotile tr talc tr scawtite (?)
MCS-5	NaCl xonotlite scawtite diopside tr chrysotile	MCS-15	NaCl xonotlite diopside tremolite (?) talc unknown d = 1.895, 1.634, 1.602
MCS-2	NaCl xonotlite scawtite tr chrysotile tr talc tr diopside	MCS-12	NaCl diopside xonotlite chrysotile talc tr truscottite (?) tr scawtite
MCS-3	NaCl scawtite xonotlite talc tr quartz tr diopside	MCS-13	NaCl truscottite (?) quartz diopside talc xonotlite scawtite (?) unknown d = 1.884, 1.880
MCS-4	NaCl quartz scawtite tr xonotlite tr talc	MCS-14	NaCl quartz truscottite (?) talc diopside xonotlite tr scawtite (?)

would be expected. Diopside is absent in the MCS-11 (1) mixture, predominant in MCS-15 (5) and then decreases from MCS-12 (2) to 14 (4).

The greatest differences among these product phases are: the absence of scawtite in the oxide mixtures; and the relatively minor role of diopside

Table 4. Comparison of product phases in cement and oxide pastes hydrothermally treated in deionized water at 400°C and 68.9 MPa for 7 days.

Mixture	Class J Cement + Minusil + MgO	Mixture	Oxides
MCS-1	xonotlite calcite chrysotile tr monticellite	MCS-11	monticellite diopside xonotlite unknown d = 2.136 tr quartz tr talc tr chrysotile
MCS-5	xonotlite calcite tr chrysotile tr talc	MCS-15	diopside xonotlite talc tr chrysotile tr tremolite (?) unknown d = 1.877
MCS-2	xonotlite talc tr diopside tr β -C ₂ S tr calcite	MCS-12	xonotlite talc diopside tr truscottite (?) tr tremolite (?) unknown d = 1.945
MCS-3	xonotlite talc tr diopside tr chrysotile tr quartz	MCS-13	talc xonotlite diopside quartz tr truscottite (?)
MCS-4	xonotlite talc quartz diopside tr tremolite unknown d = 3.142	MCS-14	talc quartz xonotlite truscottite (?)

in the cement mixtures compared to a major presence in the corresponding oxide mixtures.

Deionized Water: 400°C Curing (Table 4) CSMH System

The oxide mixtures again show greater variety of reaction products. Monticellite and diopside dominate MCS-11, compared to the presence of xonotlite and chrysotile in the equivalent cement mixture (MCS-1). Xonotlite remains fairly constant throughout the range of cement mixtures; chrysotile

is most prominent in the silica-poor mixtures (MCS-1) and decreases as SiO_2 increases. Calcite, which is a by-product of the CaCO_3 in the Class J cement, seems to remain fairly constant, showing a slight reduction as the SiO_2 content of the mixture increases (400°C is above the upper stability limit for scawtite; Harker, 1965). Talc increases with SiO_2 content, complementing the decrease of chrysotile.

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

Again, it seems that structural and kinetic factors dominate in controlling these early stage reaction products. The hydration of $\beta\text{-C}_2\text{S}$ (plus quartz) generates xonotlite, while the corresponding oxides (CaO , MgO , SiO_2) form diopside and talc more readily. Possibly, xonotlite is the metastable intermediate phase; previously reported work with 63- and 96-day mixtures with cements as starting material still contain mixtures of xonotlite, diopside and chrysotile.

Saturated NaCl: 400°C Curing (Table 5) CSMH System

Diopside, talc, quartz, and NaCl dominate the phase assemblages present from oxide-based mixtures. Talc and unreacted quartz increase as the mixtures become more silica-rich. Talc becomes predominant in the MCS-12 to 14 mixtures, while diopside decreases slightly as the mixtures become silica-rich. Monticellite appears only in MCS-11, which is the most silica-poor mixture, while NaCl remains fairly constant throughout. Xonotlite plays a relatively minor role. The lack of xonotlite in these mixtures (oxides and NaCl as brine) seems to support our previous contention that the assemblage xonotlite + chrysotile is a metastable intermediate phase assemblage at 400° and 10,000 psi, and would eventually be replaced by diopside (+ H_2O).

Contrasted with the oxide mixtures, the results of cement-based mixtures show some differences. For example, in cement-based mixtures, diopside occurs predominantly in mixtures MCS-1 and 5; xonotlite predominates mixtures MCS-2, 3, and 4. Unreacted quartz is confined to mixture MCS-4. Monticellite again appears only in MCS-1 and talc increases as the mixtures become more

Table 5. Comparison of product phases in cement and oxide pastes hydrothermally treated in saturated brine at 400°C and 68.9 MPa for 7 days.

Mixture	Class J Cement + Minusil + MgO	Mixture	Oxides
MCS-1	diopside monticellite NaCl tr calcite (?) tr quartz	MCS-11	diopside NaCl monticellite quartz unknown d = 2.950, 1.925, 1.918 tr scawtite (?)
MCS-5	diopside NaCl tr calcite	MCS-15	diopside NaCl tr xonotlite tr talc unknown d = 3.110
MCS-2	xonotlite NaCl diopside talc calcite tr tremolite	MCS-12	diopside talc NaCl truscottite xonotlite unknown d = 3.314, 2.350, 1.880
MCS-3	xonotlite talc diopside NaCl tr calcite unknown d = 3.850	MCS-13	NaCl diopside talc quartz tr xonotlite unknown d = 3.853, 2.139
MCS-4	NaCl quartz xonotlite diopside talc tr calcite	MCS-14	NaCl diopside quartz talc tr xonotlite unknown d = 1.877

silica rich--talc reaches a maximum in mixtures MCS-2 and 3. The latter results suggest either that the assemblage, diopside-monticellite, may be stable at 400°C and 10,000 psi; or NaCl affects the equilibria. An alternative is that, at lower temperatures, there is a kinetic barrier to the development of diopside, with the production of xonotlite + chrysotile as an intermediary.

The cement-based primary reaction is:

An alternative reaction, probably stable at the highest temperatures, is:

The structural control of $\beta\text{-Ca}_2\text{SiO}_4$ may favor the former reaction as an intermediate even at the higher temperatures.

The System CASH

Characterization, stability relationships, and phase equilibria studies within the CASH system showed that the addition of 10 to 45 percent boehmite ($\text{AlO}\cdot\text{OH}$) to CaO-SiO_2 in the presence of excess H_2O affects the stability of the calcium silicate phases formed. Two calcium aluminate cements, Brands S and R, were cured hydrothermally. These experiments showed the Brand S cement mixture had most favorable properties at the adjusted composition near anorthite, whereas Brand R had the most favorable strength properties when the pure cement was used. Experimentation is continuing with use of retarders to control pumping time.

Polishing Technique

A new technique for polishing cured samples of cement paste prior to microhardness studies is summarized as follows:

- (1) All specimens must be washed in an ultrasonic cleaner prior to each polishing step. This is more important for cement samples since numerous single pores are capable of holding and transferring the polishing compound from one stage of polishing to another, thereby destroying the polish.
- (2) The weight on the polishing arm should be reduced to approximately 1/2 pound. The cured cement pastes have a very fine-grained character compared to the Ca(OH)_2 crystals. Minimizing the load inhibits plucking of coarser size fractions.
- (3) Diamond paste was found to be a superior polishing agent (with oil lubricant). Polishing time for each of the 10, 3, 1, and $0.25\text{ }\mu\text{m}$ -sized diamond paste should be approximately 5 minutes, to obtain a uniform mat

surface for each size. (Ultrasonic cleaning is essential between steps.) Al_2O_3 should not be used as a polishing or buffing compound because it tends to add relief to the surface by polishing out the softer areas of the cement paste sample.

Preliminary examination of the feasibility of using a new technique for improving polishing techniques as a means of evaluating cements has been undertaken. Microhardness measurements were made using the Vickers Miniload Hardness Tester. Several Portland cement samples were tested in addition to a hydrothermally cured sample of calcium aluminate cement (HYD-21). The mean for the microhardness using the method described in previous quarterly reports and using the new technique was about 50 kg/cm^2 . The standard deviation, however, decreased from 10 for the old technique to 3 for the new technique. This may have been due to unequal length of the diagonals of the indentations using the "old" method. The equal diagonal indentations gave reproducible results ($\pm 2.5\%$). The shape of the diamond indentation varied considerably. When the diagonals were unequal, crushing and gouging of the surrounding surface area were observed and the diamond shape was distorted. Both the average of the perfect diamond indentations and the frequency of the poorly formed indentations should be reported and compared. Static indentation tests should be used in conjunction with scratch hardness tests to look at the relative hardness over larger areas. It is concluded that a good polished surface is required to make meaningful measurements.

4. PROPERTIES

Viscosity

Viscosity measurements on cement-paste slurries increased with time for all samples except for the Class J oilwell cements, which decreased in viscosity with time. An increase in blending speed decreased the viscosity also, with rotor speeds on a Haake Rotoviscometer, RV-3. The viscosity of the oilwell cement with $5 \mu\text{m}$ Minusil and MgO decreased into a more pumpable mixture when calcined metachrysotile was mixed with the cement. A summary of the strength and other physical properties associated with the latter sample mixtures are given in Table 6.

Table 6. Property measurements for a Class J cement mixed with calcined chrysotile. See Figure 2.

Sample Number	790002	790003
curing conditions	236°C; 1 day deionized water	236°C; 1 day deionized water room temp to operating temperature time = total of 2 days 236°C; 7 days 20% NaCl solution
w/s; w/c	0.39; 0.63	0.39; 0.63
Bond strength	4 MPa (575 psi)	7 MPa (1025 psi)
Permeability:		
nitrogen gas flow extrapolation (darcys)	6.5×10^{-7}	8.0×10^{-9}
pressurized water (darcys)	5.0×10^{-7}	1.0×10^{-4}
Stable Phases:	forsterite quartz (unreacted) calcite tr β -C ₂ S	scawtite NaCl forsterite

Permeability and Strength Properties

Samples prepared with the calcined chrysotile* and cured for 24 hours had a low gas permeability, extrapolated by the Klinkenberg extrapolation, and also had low water permeability (see Figure 2). Pressurized nitrogen gas was forced through the sample three hours after drying at 110°C (6.5×10^{-7} darcys) and then after 19 days of drying at 110°C (1.2×10^{-6} darcys). Water was forced through the sample at 10.3 MPa (1500 psi); approximately the same permeability value was determined. After an identical sample was cured first in deionized water then cured in a 20 percent NaCl solution, the

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

Figure 2. Permeability measurements made with pressurized nitrogen gas up to 800 psi.

gas permeability was extremely low (10^{-9} darcys) and the water permeability was approximately 10^{-4} darcys. The 24-hour sample far exceeds the criteria set at the beginning of this study of less than 0.1 millidarcy permeability to water.

Bond strengths for these preliminary samples exceed the criteria set at the beginning of the study (bond strengths greater than 10 psi).

Bond strengths will be reported next month on cured calcium aluminate samples which cured for 8 days at 395°C and 34.5 MPa (5000 psi).

5. CONCLUSIONS

A comparison between the oxide and the cement product phases after hydrothermal curing for 7 days at 300 and 400°C at 68.9 MPa (10,000 psi) showed a greater number of phases present in the oxide mixtures (presumably final equilibrium was not attained). The oxides, with smaller particle sizes, are assumed to be more reactive than the cement. However, the cement-based reactions were complicated by the presence of carbonated lime in the Class J cement, forming scawtite. Kinetic factors are important in the phase formation, and some of the shorter-term results are still difficult to interpret. Hydration products of previous 63- and 98-day runs at 400° and 68.9 MPa still contained the combination chrysotile-xonotlite. However, there is still some question as to whether the alternate pair, diopside-monticellite (+ H_2O), may be more stable; or if indeed precise P-T conditions can be defined for transition from one stable pair to the other. The final compositional concern is the effect of minor components (or NaCl) on the stable phases.

The property measurements of the cement-based mixtures at the composition of Mixture 19 shown in Figure 1 meet the criteria of bond strength, permeability, and long-term strength after hydrothermal curing. The viscosity for samples made with the calcined chrysotile was more pumpable than that with oxides.

The property measurements of the calcium aluminate cement-based mixtures indicate adequate strengths. More fluid mixtures will be tested for the retention of strength properties.

6. REFERENCES

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Appendix 5

BNL CONTRACT 418691-S

PHOSPHATE BONDED GLASS
CEMENTS FOR GEOTHERMAL WELLS

Technical Report No. 7
January to March, 1979

from

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I. INTRODUCTION

This report covers the work completed on contract 418691-S between January 1, 1979 and March 31, 1979. The tasks performed fall into three major areas of activity.

The first area involves the solubility of silicate glasses in phosphate solutions. This area is critical to the type of geothermal cements being investigated in this contract because a glass is the major starting material for the cement. It is the interaction of the glass with a phosphate liquid that forms the cement. If the glass is insoluble in the liquid phase, no cement will result. If there is a major interaction between the glass and the liquid a cement may form so rapidly that no set time will be available for emplacement. Understanding the solubility behavior of the glasses is basic to the selection of a geothermal completion cement.

The second group of experiments is equally important to cement design and involves the equilibrium phase relations between aluminum oxide, calcium oxide and phosphate solutions. The glasses release cementing constituents to the phosphate liquid. Just which constituents should be added to the glasses is determined by these equilibrium studies. The ratio of calcium oxide to aluminum oxide which will react with various phosphate solutions to yield stable compounds (and therefore could form a stable cement) is the resulting data obtained from the equilibrium studies.

The third phase of the work involves the testing of cements which have been designed using the data from the first two sections. The glass composition which is receiving the major attention at this time is the 7% Na_2O :24% CaO :24% Al_2O_3 :45% SiO_2 . Preliminary tests have shown that this material sets in several hours and appears to have some high temperature stability. Quantities sufficient for further testing are being prepared and longer term tests are being initiated.

II. GLASS SOLUBILITY

In a phosphate cement system, the glass phase is a carrier of reactive constituents. Knowing the corrosion rate of the glass and the mechanism by which the glass is broken down by the phosphoric acid is important to the design of cements. Acid alkali or even water is sufficient to deteriorate some glass.^(1,2) The degree of attack is controlled by the concentration and temperature of the corrosive agent, and also by the composition of the glass. The other factors which affect the extent of deterioration are the glass configuration (i.e. bulk or powder) and the influence of the reaction products on the glass surface. Some of the ways in which corrosion can occur are⁽³⁾: (i) creation of a leached surface layer due to preferential dissolution, (ii) exposure of fresh glass surface on account of continuous dissolution or (iii) formation of new surface compounds which inhibit further corrosion.

Pure silica, a major component of the cement glasses is only sparingly soluble in acidic solutions⁽⁴⁾. There is not much change in silica solubility as the pH of the solution is decreased. In alkaline solutions, silica dissolves because of the formation of soluble sodium silicates. The silica solubility in alkaline solutions increases with increase in pH⁽⁵⁾.

Aqueous solutions and acidic solutions will react with many silicate glasses so that an alkali metal ion is replaced by a proton⁽⁶⁾. The solubility of some silicate glasses is not affected greatly by the acidity of the solutions. In general, if the SiO_2 content is low then attack by the acids is increased. In certain silicate glasses, the basic ions are leached to yield a silica rich surface layer which resists further corrosion⁽⁷⁾. Though the alkali and basic oxide components are replaced by H^+ , the Si-O-Si bonds which constitute the original glass backbone structure are relatively unaffected.

On the other hand, basic solutions will react with silicate glasses to a greater extent than neutral or acid solutions⁽⁸⁾. This is due to the breaking of Si-O-Si chains to form Si-OH and Si-O-Na groups^(9,10,11). If a glass surface is leached with acid the resistance to attack of the surface may increase, but this is not observed if the leaching is done with alkali⁽¹²⁾.

Under certain conditions, neutral corroding solutions like water will increase in basicity as a result of the dissolution of alkalis from the glass⁽¹³⁾. This will accelerate the corrosion of the glass surface. At moderate temperatures fused silica is unaffected by water for long periods of time

while glasses containing alkali or alkaline earth metal can undergo severe decomposition.

The interaction of water with alkali ion bonded in the glass has been represented by Charles by the following equation⁽¹⁴⁾:

where R represents the alkali ion. For the glasses studied in this program, R represents the calcium and aluminum ion. These released ions react with phosphate in solution to form cementing phases. The oxygen alkali bond is broken and a non-bridging hydroxyl ion is formed. The dissociation of the water molecule produces a free hydroxyl ion.

This hydroxyl ion breaks the very strong Si-O-Si bond giving another silanol bond and a non-bridging silicon oxygen bond.

This non-bridging silicon oxygen bond is capable of dissociation another water molecule and liberating a free hydroxyl ion which can break another Si-O-Si bond.

There is excess hydroxyl ion formed by these reactions in neutral or basic solutions. This increase in pH makes the glass dissolution process autocatalytic in aqueous solutions. The dissolution rate goes on increasing but only up to a certain limiting value⁽¹⁵⁾. The pH does not increase indefinitely because of formation of silicate ionic groups $-\text{Si}(\text{OH})_6^{-2}$. The formation of these groups at high pH act as a buffer by re-

moving hydroxyl ion from the solution. For phosphoric acid solutions a more representative equations for the corrosion process can be written as follows:

The phosphate ions are H_2PO_4^- , $\text{HPO}_4^{=}$ and $\text{PO}_4^{\equiv}$. The amount of each depends on the dissociation constants for the acid. When the concentration of R^+ become high enough, phosphates which are stable under the conditions of leaching will precipitate. Such phases as monetite, berlinite, apatite, augellite, hydroxyapatite and crandallite have been found by this study to be stable at 200°C. These phases will form the cementing matrix. In the corrosion studies, these precipitation reactions are not considered because the experiments were designed to give infinite dilution conditons. The possible exceptions are when the 50% phosphoric acid is used. As seen below, there is some evidence that precipitated phase interferes in this case.

Spinodal Decomposition

Although separation of a glass into more than one amorphous phase was postulated many years ago, it was established as a common phenomenon only in the past twenty years. Furthermore, during this period it was determined that most glasses display this behavior and it is the basis for understanding many of the properties of glass

The miscibility gap is divided into two thermodynamic regions depending on the value of the second derivative

of the solution free energy with respect to concentration. If second derivative is positive then the solution is in a metastable state; if it is negative then the solution is unstable⁽¹⁶⁾. This leads to a phase separation in the glass⁽¹⁷⁾. The separation is on a scale of 30 to a few hundred Å⁽¹⁸⁾. This could happen in the normal course of cooling the melts as it does for sodium borosilicate glasses⁽¹⁹⁾.

Phase separation occurs by one of the following mechanisms⁽²⁰⁾: (i) nucleation and growth or (ii) spinodal decomposition. All glass is metastable with respect to the crystalline phase which should form. If the glass is in a system which shows phase separation, the single phase solution can also be metastable with respect to two amorphous phases. Spinodal decomposition theory predicts that the single phase solution can be unstable with respect to two phase in a certain composition range. When in the metastable region then decomposition occurs by nucleation and growth of a dispersed phase in a matrix phase. If the glass is in the unstable region then spinodal decomposition takes place. Phase growth occurs by gradual increase in differences of composition. Both the phases will be continuous and inter-connected. The continuity of the two phases is maintained only if the volume fraction of the minor phase is greater than 15%⁽²¹⁾. If the volume fraction becomes less than 15%, the structure will be similar to that obtained by nucleation and growth mechanism. Whether having separated by a spinodal mechanism or not, many glasses have been shown to be more than single phase materials

after they have been cooled to room temperature.

The details of making fibers of various compositions and measuring their corrosion in various phosphoric acids has been given in previous reports. Shown in Figures 1 and 2 are the corrosion rates of various glasses in 30% H_3PO_4 solutions. In Figure 1, the results for the ternary glasses from the system $\text{CaO-Al}_2\text{O}_3$ and SiO_2 are shown. The glasses have equal amounts of CaO and Al_2O_3 and the SiO_2 content varies from 60 percent to 40%. Between these values, there is a change from "no observed attack" to "severe decomposition." The same trend is observed in Figure 2 for the quaternary glasses of the system $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$. All of these glasses contain 7.0% Na_2O . CaO and Al_2O_3 contents are kept equal and SiO_2 is varied. Again, the 60% SiO_2 glass shows no deterioration and the 40% glass dissolves in a matter of minutes. This sudden change in deterioration can be explained by phase separation. As outlined above it is the exchange of sodium, calcium and aluminum ions with protons that cause the deterioration. If the glasses are phase separated then the high silica glasses (60% SiO_2) will be made up of a continuous high silica matrix with the ions concentrated in a second phase which is dispersed in the matrix phase and therefore isolated from the corrosive liquid. The lower silica glasses are separated into a ion rich matrix which is soluble and a dispersed silica-rich phase which goes into colloidal suspension as the continuous phase is dissolved. If this explanation is correct there should be a range of compositions in which the silica-rich and ion-rich phases are present in roughly equal amounts and are both con-

Figure 1. Dissolution rate of ternary glass in 30 wt. % H_3PO_4 as a function of silica content.

Figure 2. Dissolution rate of quarternary glass in 30 wt. % H₃PO₄ at 40°C as a function of silica in the glass.³

tinuous and therefore exposed to the liquid. This should lead to an extraction of the ion-rich phase and the glass should have the silica-rich phase present as a continuous surface film. The behavior is observed for the 53% silica glass. This glass is totally replaced by a silica-rich film phase.

This data has now been used for the selection of glasses which will be tested for their cementing properties. It is shown later in this report that only those glasses showing an appreciable corrosion rate will form cements. Further, initial studies show that the setting time of the cement is a direct function of the corrosion rate of the glass.

III. EQUILIBRIUM STUDIES

The equilibrium studies concentrated on the phases which would be stable under geothermal conditions in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. The four main related ternary systems $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$, $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$, $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$, and $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ in the quaternary system have either been defined in previous reports or have been studied and reported on by other workers. The first two systems were constructed and presented in Technical Report No. 4 under this project. The previous studies^(22,23) on the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ showed that there are no ternary compounds in the system. M. S. Crowley⁽²⁵⁾ reported that the hydrogarnet C_3AH_6 is the only stable phase in the system $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ at relatively high pressure at 200°C. However, he also mentioned that if traces of foreign ions exist in the samples, C_2AH_6 will be formed.

D. Roy in her study of geothermal cement stability has reported the occurrence of the hydrogarnet C_3AH_6 at 380°C in some low silica hydrothermal runs. This is above the temper-

ature that Crowley reports for the stability of C_3AH_6 but the run is made at a lower pressure. Both authors report $C_4A_3H_3$ at temperatures of $400^\circ C$ ⁽²⁴⁾.

Due to the lack of available experimental information on the quaternary system $CaO-Al_2O_3-P_2O_5-H_2O$ at $200^\circ C$ this isothermal is being investigated. A literature review of the compounds which occur as minerals has indicated some quaternary compounds which may be encountered in this study. There are five related compounds which are listed in Dana's system of Mineralogy⁽²⁶⁾. They are: Tavistockite $Ca_3Al_2(PO_4)_3(OH)_3$. Montgomeryite $Ca_4Al_5(PO_4)_6(OH)_5 \cdot 11H_2O$, Overite $Ca_3Al_8(PO_4)_8(OH)_6 \cdot 15H_2O$, Davisonite $Ca_3Al(PO_4)_2(OH)_3 \cdot H_2O$ and Crandallite $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$. P. G. Embrey and E. E. Fejer⁽²⁷⁾ reported that Tavistockite probably is an apatite or fluoroapatite. The original analysis was made on a mixture of apatite and kaolinite. Paul B. Moore⁽²⁸⁾ and Luca Fanfau et al.⁽²⁹⁾ found the presence of Mg in Montgomeryite crystal from their electron probe and laser microprobe analysis. Paul B. Moore⁽³⁰⁾ also pointed out that the formula of Montgomeryite should be $Ca_4Mg(H_2O)_{12}[Al_4(OH)_4(PO_4)_6]$. Paul B. Moore and T. Araki⁽³¹⁾ recommended that the chemical formula of Overite be changed to $[Mg(H_2O)_4]_2[CaAl_2(OH)_2(PO_4)_4]$ owing to an erroneous original formula. Thus only Davisonite ($C_6AP_2H_5$) and Crandallite ($C_2A_3P_2H_6$) appear to be verified compounds of the quaternary system. In addition, Paul B. Moore⁽³²⁾ found a new Calcium Aluminophosphate hydrate $Ca(H_2O)_2[CaAl_2(OH)_4(PO_4)_2]$ which he named foggite. It was discovered in rocks from North Groton, New Hampshire.

In order to establish the phase relation in quaternary system, four planes were chosen for investigation. They are: 25% CaO: 75% Al_2O_3 - P_2O_5 - H_2O , 50% CaO: 50% Al_2O_3 - P_2O_5 - H_2O , 75% CaO: 25% Al_2O_3 - P_2O_5 - H_2O , and the 90% H_2O planes. The reason for choosing the last one is based on the characteristics of solid-liquid equilibria. All phases in the system which show equilibrium with water must have tie lines which pass through this plane. Therefore, we feel this is the best way to define the stable hydrate in the system. A diagram representing planes of investigation is shown in Fig. 3.

The experimental procedures have been described in previous reports. The sealed pyrex ampules are used for reactions. For the first three planes, CaO- Al_2O_3 mixture at specific proportions were prepared by grinding to a powder the pellets which consist of exact amounts of CaO and Al_2O_3 which had been fired at 1200°C for at least 8 hours. The H_3PO_4 was diluted to make the solutions which are reported as P_2O_5 and H_2O . For the 90% water plane, the starting materials for all runs were Al_2O_3 , $\text{Al}(\text{PO}_3)_3$, CaO, $\text{Ca}_3(\text{PO}_4)_2$, 75% CaO: 25% Al_2O_3 , 50% CaO: 50% Al_2O_3 , and 25% CaO- 75% Al_2O_3 , made up to exact composition of required points on CaO- Al_2O_3 - P_2O_5 plane after using material balance to calculate the proportions accurately. These compositions are shown in Fig. 4. Samples were made up of 10 wt.% solid powder and 90 wt.% distilled water and, then, the above mentioned procedure was followed.

Figure 3. Planes under investigation in the system
 $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$.

Figure 4. Points chosen on the $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ plane for 90% water plane.

The results of system 50% CaO: 50% $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ were presented in the former report. The firing made in the 25% CaO: 75% $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ are shown in Fig. 5 and are currently being analyzed. The results of 75% CaO: 25% $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ are presented in Table 1. From the available data which have been collected so far, the phase relations at 200°C in the system CaO- $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ can be constructed as shown in Figure 6. The compatibility join between monetite and berlinite has been established and a large part of the tetrahedron is dominated by the three phase region monetite + berlinite + solution. The solutions are phosphoric acids in which Ca^{++} and Al^{+++} are dissolved up to several percent at higher phosphate compositions. At low phosphate compositions, calcium and aluminum are only sparingly soluble. The species in the solutions are not known there are probably ion phosphate complexes present.

At high phosphate concentrations, Crandallite is the phase in equilibrium with the liquids. The 1.1.3 compound is also observed but it is not known if this phase is stable or if it forms on cooling the ampules to room temperature. This suggests the presence of an invariant liquid which will coexist in equilibrium with Crandallite, berlinite and monetite. If that 4-phase region exists then there must also be a three phase region with equilibrium between Crandallite, a solution and either monetite or berlinite. These studies are continuing.

Figure 5. Compositions of firing made in the system
CaO-Al₂O₃-P₂O₅-H₂O.

Table 1
Results of Experiment Made in the System
CaO-Al₂O₃-P₂O₅-H₂O at 200°C

No.	Composition Wt%			Time (hrs)	Phases Present
	75%CaO: 25% Al ₂ O ₃	P ₂ O ₅	H ₂ O		
75-1	2.0	9.3	88.2	92	AlPO ₄ +CaHPO ₄ +Liq
75-2	4.0	9.6	86.4	92	AlPO ₄ +CaHPO ₄ +Liq
75-3	6.0	9.4	84.6	138	AlPO ₄ +CaHPO ₄ +Liq
75-4	8.0	9.2	82.8	98	AlPO ₄ +CaHPO ₄ +Liq
75-5	10.0	9.0	81.0	98	AlPO ₄ +CaHPO ₄ +Liq
75-6	2.0	29.4	68.6	138	Liq
75-7	4.0	28.8	67.2	69	AlPO ₄ +Liq
75-8	6.0	28.2	65.8	138	AlPO ₄ +Ca(H ₂ PO ₄) ₂ ·H ₂ O* +CaHPO ₄ +Liq
75-9	8.0	27.6	64.4	142	AlPO ₄ +CaHPO ₄ +Liq
75-10	10.0	27.0	63.0		Loss of sample
75-11	2.0	49.0	49.0	48	Liq
75-12	4.0	48.0	48.0	48	Liq
75-13	6.0	47.0	47.0	120	CaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O +Ca(H ₂ PO ₄) ₂ ·H ₂ O*+Liq
75-14	8.0	46.0	46.0	144	CaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O +Ca(H ₂ PO ₄) ₂ ·H ₂ O*+Liq
75-15	10.0	45.0	45.0	120	CaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O +Ca(H ₂ PO ₄) ₂ ·H ₂ O*+Liq

* Probably formed on cooling

Figure 6. Phase relations at 200 C in the system
 $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$.

IV. CEMENT TESTS

The quaternary glasses containing 7% Na_2O were mixed with 30% phosphoric acid to determine if a cement would be formed and if so, at what time it would set. The 60% SiO_2 glass does not set at all, while the 55% SiO_2 glass takes about 3 hours. The setting time is determined by the Gilmore needle test at certain time intervals; if the pin does not cause any mark on the cement, then the cement has set. Using the same method, the setting time for 40%, 45% and 50% glasses are determined as 10 mins, 15 mins, and 25 mins respectively.

The cements formed as described above were submerged in water at room temperature for 5 days. The cements do not disintegrate or deteriorate due to this exposure. They appear to be totally resistant to water at room temperature.

Each of the cement samples (55%, 50%, 45% and 40% SiO_2 quaternary glass frit as starting material) is placed in a separate thick walled pyrex tube and water is added so that they are totally immersed. The ends of the tubes are sealed so that they are completely air-tight; each of the glass tubes is then placed inside a bigger iron tube whose ends are bolted. This assembly is then placed inside an oven at 140°C . After 48 hours, inside the oven, the tubes are removed and allowed to cool. Each tube is then broken open and the cements examined to check for their stability. A summary of the findings is given in Table 2.

Table 2

Stability of Phosphate Cements at 140°C.

Cement Sample	%SiO ₂ in the glass	Strength Characteristics
S ₂	55	Some of it has become powder inside the tube and settled at the bottom. The sample becomes powder on applying slight pressure.
S ₄	45	Hard and resistant; does not become powdery.
S ₅	40	Does not deteriorate in water but crumbles into powder on application of slight force; not strong at all.
S ₃	50	Does not deteriorate in water but can be broken into pieces with little applied force.

Based on these preliminary findings a program has been started to melt a pound of the 7% Na₂O: 24% CaO: 24% Al₂O₃: 48% SiO₂. This glass will be ground and seived through 200 mesh screens and the powder will be used for a more extensive testing program.

V. FUTURE PLANS

This contract is now entering the final quarter. Most of the work will be directed at defining the properties of cements which will be selected on the basis of the equilibrium studies and the solubility studies. The equilibrium studies will be carried to conclusions and some effort will be expected to determine if silica from the glass phase enters the cementing reaction at hydrothermal temperatures and pressured.

Cement tests will be made to obtain information on stability at 200°C in water. Strength measurements will be made as a function of liquid to solids ratios and the effect of fillers such as silica will also be determined. Information on the compatability of the cements with steel will also be obtained during this period and a final report for the project will be prepared.

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

TECHNICAL PROGRESS REPORT NO. 6
January - March 1979
SwRI Project No. 02-5083
BNL Contract No. 427964-S

to

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

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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 sixth quarterly technical progress report includes work accomplished during the period January - March 1979. 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, permeability to water, thermal expansion /contraction properties, and corrosion properties.

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 sixth quarter of Brookhaven National Laboratory Contract No. 427964-S at SwRI.

During the period of January 1 to March 31, 1979, 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 and long-term aging have continued.

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

We have continued to search for the optimum formulation for use at 316°C and above. Table I gives the various recipes which will be useful at these temperatures. Consistometric tests have shown that these recipes will give as long as three hours pumping time at 316°C. We have made the decision to go with the aluminum oxide and zirconium oxide at temperatures up to 400°C.

TABLE I
SwRI HYDROTHERMAL CEMENT FORMULATIONS
FOR USE AT 316°C AND HIGHER

<u>SPECIMEN SERIES</u>						
<u>Ingredients</u>	<u>#60</u>	<u>#70</u>	<u>#80</u>	<u>#90</u>	<u>#100</u>	<u>#110</u>
Sand		50			50	
Flour	50	25	50	50	25	50
Britesil	10	10	10	10	10	10
Anhydrous Sodium Silicate	10	5	10	10	5	10
Bentonite	.5	3	.5	.5	3	.5
Al (OH) ₃	7					
Al ₂ O ₃		5				
TiO ₂					8	
ZrO ₂			7			
La(OH) ₂						7
LaO ₂				7		
H ₂ O	23	18	23	23	20	23

B. Physical Properties Evaluation

1. General

We have continued to perform mostly routine, long-term exposure tests on SwRI 315°C and 400°C hydrothermal cements in steam and simulated brines. The "static" steam condition is provided by maintaining sufficient water in the autoclave to give a fully saturated vapor condition. Other specimens are cured partly submerged in synthetic brine. Strength tests are being performed on the cured specimens.

Two formulations have been chosen for use at well temperatures above 300°C.: aluminum oxide or zirconium oxide. Aluminum hydroxide can be used as the activator at temperatures of up to 316°C. Where necessary, in the future, if a longer pumping time than 3 hours might be required, we can use lanthanum or vanadium oxides as activator. We can also increase the pumping time, when using the $Al(OH)_3$ and ZrO_2 , by adding some minus 60 mesh sand. Specimens cured for 28 days have been tested for compressive and bond strengths, and for permeability to water. The following sections report further on these tests.

2. Compressive Strength

One-inch cylinders and two-inch cubes have been made from several formulations, cured for periods of 14 and 28 days, and tested for compressive strength. Results of these tests after specimens were cured and aged in a saturated steam and/or brine environment are as shown in Table II. The Table is a summary of several compressive strength tests performed on various recipes and cured at the indicated times and temperatures. Each specimen number and type is an average of two or more specimens made according to the recipes shown in Table I.

TABLE II
COMPRESSIVE STRENGTHS

<u>SPECIMEN</u>	<u>ACTIVATING AGENT</u>	<u>CURE TEMP. °C</u>	<u>CURE TIME Days</u>	<u>COMPRESSIVE STRENGTH (psi)</u>
601A	Al(OH) ₃	316	15	4915
601B	"	"	"	3124
601C	"	"	"	3288
601D	"	"	"	2918
601E	"	"	"	4932
601F	"	"	"	5015
602A	Al(OH) ₃	316	14	4193
602B	"	"	"	3165
602C	"	"	"	2840
602D	"	"	"	3764
602E	"	"	"	4604
602F	"	"	"	5097
603A	Al(OH) ₃	316	28	5657
603B	"	"	28	5056
603C	"	"	28	3799
603D	"	"	28	5038
603E	"	"	28	5974
603F	"	"	28	4275
604A	Al ₂ O ₃	400	7	460
604B	"	"	7	324
604C	"	"	7	587
604D	"	"	7	844
604E	"	"	7	1202

NOTE: Series 604A thru 604E were not sufficiently cured after 7 days in autoclave.

TABLE III
BOND STRENGTH

<u>SPECIMEN</u>	<u>ACTIVATING AGENT</u>	<u>CURE TEMP. °C</u>	<u>CURE TIME Days</u>	<u>BOND STRENGTH psi</u>
6010A	Al(OH) ₃	316	7	395
6020A	"	"	15	1071
6020B	"	"	"	641
6030A	"	400	14	2143
6030B	"	"	"	395
6040A	"	316	28	2424
6040B	"	"	"	403

4. Permeability to Water

Permeability tests were made on a number of specimens cured at 316°C and 400°C. These tests were made on a cement permeameter similar to that shown in the American Petroleum Institute (API) Method RP10B, Section 9. Specimens were made by pouring the cement mix into a steel mold which was capped top and bottom, and cured in the autoclave. All of the specimens were made from basic high temperature formulation using aluminum hydroxide as the activator. Some variation was used in the mix design, usually in the amount of anhydrous sodium silicate, or by the addition of other materials. These variations have been made in an attempt to bring the permeability down to a maximum of 0.1 millidarcy (md). Thus far we have not been too successful with the cylinders cured at 316°C and 400°C. We are still attempting to find the cause of this apparent loss of near impermeability we obtained at temperatures below 200°C. Results of some of these tests are given in Table IV.

TABLE IV
PERMEABILITY TO WATER

<u>NOTES ON FORMULATIONS</u>	<u>CURE TEMP. °C</u>	<u>CURE TIME Days</u>	<u>PERMEABILITY (MILLIDARCYs) (at abt 40 psi)</u>
#1: Cement reacted w/spacers	316	2	>100
2: "	"	8	>200
3: "	"	8	>100
4: Bonded well to steel	"	2	>100
5: Partly broken in top	"	2	>100
6: Bonded well to steel	"	14	>200
7A: Reduced A. Sod. Sil.	316	7	80
7B: "	"	7	60
8: Add ASA and pyrophos.	316	6	>200
9A: Decreased Sand -Inc. Silica Flour	100	1	.01
9B: "	100	1	.005 } 80 psi
10A: Add ZnO	316	5	>200
10B: Normal Mix	316	5	193
10C: Add Al ₂ O ₃	316	5	Not set
10D: Add ZrO ₂	316	5	Not Set
11A: ZnO subst. for Al(OH) ₃	316	7	Leakage at wall
11B: Add ZnO	316	7	1ml/sec.
11C: ZrO ₂ subst for Al(OH) ₃	316	7	Not set
12A: Add ZnO & bentonite	316	4	14
12B: "	316	4	19
12C: "	316	4	17
13: average of 3 additions as in 12	400	3	15
14: ZrO ₂ & bentonite additions	400	4	Not set

5. Thermal Properties

A number of specimens are being cured and aged for 28 days in steam at 316°C and at 400°C for the purpose of measuring their thermal properties. At the time this report was written the 28 day aging had not been completed.

6. Future Work

In the next quarter, many of the 28 day exposure tests should be completed on the zirconia recipe. Compressive and bond strengths will be performed on these specimens. Thermal tests should be completed also, along with the determination of the elastic moduli.

DRAFT: May 24, 1979

PRACTICES FOR PROPERTY TESTING OF GEOTHERMAL CEMENTING MATERIALS

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I. Scope

The National Bureau of Standards is under contract with the U.S. Department of Energy to verify certain properties of cementing materials which are submitted as candidates for use in the finishing operations of geothermal wells. Specimens will be set-cured in molds under water for two days at elevated temperature and pressure. Subsequently, these cured specimens will be exposed unprotected in simulated geothermal fluids for periods of one week and one month. Following each of these treatments, the following properties will be measured at room temperature and pressure: compressive strength, tensile strength by diametral compressive loading, shear-bond strength of the cement-metal interface, and cement permeability to water. Upon the basis of this survey of properties at room temperature, a priority of cementing materials will be established for further testing of select physical properties while the specimens are at elevated temperature and pressure in the simulated geothermal fluids.

II. Candidate Cementing Materials

A. Participants

Several investigators, some of whom are under contract with the U.S. Department of Energy, have been developing candidate geothermal cementing materials. Any investigator who has a candidate cementing material to submit to this property testing program will be deemed a participant.

B. Placement Ability

1. Participants will provide written certification that the slurry of each cementing material that they submit has passed the API thickening time requirement for a class J cement in a 3050 m (10,000 ft.) well depth (Table 2.2 of reference 1). This requirement specifies that the slurry must have a consistency less than 30 Bc during the initial 30 minutes of the stirring period and a consistency less than 100 Bc up to 3 hours of the stirring period.

2. The thickening time of a slurry will be measured according to the API thickening time test (section 7 of reference 2). The pressure and temperature control will follow the casing cement schedule 6g (p. 34 of reference 2) which has been extended to provide that the slurry be heated from 27 to 150 °C in 36 min (average rate of 3.4 °C/min). [Note: the task group may wish to consider a less severe pressure condition, such as the 36 MPa (5300 psi) used by Dowell (p. 105 of reference 3), rather than the 51.7 MPa (7500 psi) given in schedule 6g].

3. Participants may have these tests performed by Dowell under the conditions described in reference 4 (see attached).

C. Mixing Proportions

1. Participants will give the mass ratio of the cementing components which are to be mixed, for example: 1.00 cement, 0.40 filler, 0.025 additive, and 0.60 water.

2. They will give the slurry density, which may, for example, be determined by the method in Appendix B of reference 2.

3. They will provide the details of any special slurry mix instructions which differ from those described in section IV A below.

D. Description

1. Participants will identify each cementing component by a convenient name, for example: API class H cement, Lone Star, Dallas, Texas. (A manufacturer's name is given to identify the material and does not imply that this material is the best available).

2. Unless a cementing material is proprietary, its chemical composition and preparation should be indicated for future reference and identification, for example: 1.00 cement (0.23 SiO_2 , 0.65 CaO , $0.04 \text{ Fe}_2\text{O}_3$, $0.05 \text{ Al}_2\text{O}_3$, 0.02 SO_3 , and 0.01 MgO by mass fraction), clinkered at 1500°C , and pulverized (200 mesh); 0.40 silica flour (200 mesh); etc.

E. Shipment

1. Participants should submit before October 1, 1979 cementing materials which meet the above criteria of placement ability. Send the cementing materials, excluding water, to the attention of Ralph Krause, A355 Materials, National Bureau of Standards via, either of the following:

Commercial Carrier: Route 270 and Quince Orchard Road
 Gaithersburg, Maryland 20760

or U.S. Mail: Washington, D. C. 20234

2. Preferably, the respective cementing components should be packaged separately; and sufficient quantities should be provided to prepare at least eight liters of slurry.

3. Alternatively, if some participants prefer to premix the cementing components themselves or if these components might tend to segregate in shipping, they should provide at least eight packages of cementing material each of which will form one liter of slurry.

III. Apparatus

A. Balances

1. The prescribed quantities of cementing components will be weighed upon a pan balance which has a one kg capacity and an inaccuracy of ± 0.1 g.

2. The quantities of salts which are used to prepare the simulated geothermal fluids will be weighed upon a balance which has a 200 g capacity and an inaccuracy of ± 0.1 mg.

B. Mixing Device

1. The components of a given cementing material will usually be blended in a Waring Blender which has a two liter container and a two-speed propeller-type mixer of stainless steel, capable of rotating 4000 rpm or 10,000 rpm.

2. Also available is a Hobart N-50 mixer which has a 5 qt. stainless steel bowl with a flat beater as described in ASTM Method C305 for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency.

C. Molds

1. Specimens for the compressive and tensile strength tests will be set-cured in Pyrex tubes (20 mm OD, 1.2 mm wall thickness, and 150 mm length). Each tube will be thinly coated with silicone grease and capped with a Teflon plug, which has a one mm hole to equalize the pressure and to accommodate any thermal expansion of the slurry. [Note: This specimen diameter is deemed appropriate due to the prospect of having to handle many specimens. A constraint is the 5 cm ID of the pressure vessels that are available for the geothermal exposures.]

2. Specimens for the shear-bond strength and permeability tests will be set-cured in molds of modified, one-inch-pipe nipples of stainless steel. Commercially available nipples (7/8 inch ID, 1 3/8 inch wrench pad, and 2 1/4" length) will be sawed in half perpendicular to their longitudinal axes. The inside diameter of the resulting pieces will then be tapered in a conical fashion such that the opening at the pipe threaded end is about five per cent larger than the opening at the wrench pad end. Removeable cover plates (3 mm thick) are machined to fit the ends of these molds, so that the molds may be stacked within a pressure vessel. A one mm groove is machined across the bottomside of the upper cover plates to accommodate any thermal expansion of the slurry. Teflon sheets (0.05 mm thick) will separate the specimen and the cover plates. Some of the cover plates will have recesses to center steel rods (10 mm OD and 28 mm length) inside those molds which will be used for the shear-bond strength tests.

3. A stainless steel rod (3 mm OD and 200 mm length) will be used to puddle slurries in their molds.

D. Diamond Saw

A motorized diamond blade (6 inch OD, 0.02 inch width, 1725 rpm) will be used to saw the molded rods of set cement into specimens. Two miniature vises which are attached to a platform will secure a rod on each side of a cut. The platform will move automatically at a constant rate (0.5 mm/s) to feed the rod perpendicular to the blade, rotating in a fixed position through a bath of water.

E. Calipers

The lengths and diameters of specimens will be measured with calipers with an inaccuracy of ± 0.02 mm.

F. High Pressure Systems

1. A one gallon stirred autoclave of 316 stainless steel, which can be operated up to a maximum pressure of 21 MPa (3000 psi), will be used to set-cure cementing materials in molds which are submerged in distilled water.

2. A series of four pressure vessels of Hastelloy alloy C 276 (2 inch ID, 10 inch internal length, two top ports, and one bottom port) will be used to expose unprotected specimens of set cements in simulated geothermal fluids at pressures up to a maximum operating pressure of 60 MPa (8,700 psi). The wetted parts of all high pressure valves and fittings are also made of Hastelloy alloy C, except for the pressure lines which are made of Monel tubing.

3. A source of compressed nitrogen or argon will be available to provide pressures up to 40 MPa (5,800 psi) to all five pressure vessels.

4. A liquid metering pump with a Hastelloy alloy C 4 pump head and a tantalum diaphragm will deliver the simulated geothermal fluids with a nominal flow up to 800 ml/hr to any of the four Hastelloy pressure vessels. Being driven by an air motor, the pump can maintain a constant output pressure up to a maximum of 69 MPa (10,000 psi) by adjustment of the pressure of the air supply.

5. Bourdon gauges with Monel coils and sockets will be used to indicate continuously the pressure within each vessel to an inaccuracy of ± 0.2 MPa (30 psi). A reference gauge will serve to calibrate periodically the operating gauges. Another bourdon gauge will be used to measure the partial pressure of CO_2 over the simulated geothermal fluid reservoir with an inaccuracy of ± 0.7 kPa (0.1 psi).

6. A pressure generator of 316 and 14-4PH stainless steels is being considered to compress water in order to develop a pressure difference across a permeability specimen. This generator is a manually operated piston screw pump which can be operated up to 69 MPa (10,000 psi).

7. Whenever all liquid conditions are used in the Hastelloy pressure vessels at elevated pressure and temperature, relief valves are being considered to dump overflow fluids in the event of an inadvertent over-pressurization. [Note: The use of these valves would possibly avoid abortion of an on-going exposure; nevertheless, safety rupture discs will also be installed on these vessels].

G. High Temperature Systems

1. Nichrome wire-wound, tube furnaces are available to surround each of the five pressure vessels, the Hastelloy vessels having furnaces of the split-tube type. These furnaces will be used to heat the vessels and their contents to elevated temperatures at a rate of about 3 °C/min. The maximum operating temperature is 340 °C for the stirred autoclave and 400 °C for the Hastelloy pressure vessels.

2. A temperature controller with an adjustable proportional band, reset, rate, and approach controls will be used to operate each furnace automatically from room temperature to the operating temperature for that furnace, and to maintain the final temperature within ± 2 °C.

3. Chromel-alumel thermocouples will be used to indicate the temperature of the contents inside of each pressure vessel and the temperature at selected spots along the exterior surface of the pressure vessels. A digital voltmeter which is calibrated in degrees Celsius will be used to read the respective thermocouples to ± 1 °C.

4. The stirred autoclave is equipped internally with a water-cooling coil; the four Hastelloy vessels have externally applied water-cooling coils.

5. A constant temperature bath of stirred water will be used to hold specimens of set cements at 25 ± 1 °C preceding their property tests at room temperature.

H. Fluid Handling Systems

1. Two reservoirs of stainless steel (four liter capacity each) will store at room temperature the two simulated geothermal fluids of different compositions, equilibrated respectively under appropriate pressures of carbon dioxide. Manipulation of stainless steel valves will direct either fluid to the high pressure metering pump.

2. A pH meter will be used to monitor the acidity of the fluids in the reservoirs. Both a glass measuring electrode and a reference electrode will be mounted in a stainless steel chamber to allow pH measurement to be made at pressures up to one MPa (150 psi).

I. Load Testing Machine

A recently calibrated Tinius Olsen Electromatic Universal Testing Machine (12,000 lb load capacity) will be used to apply compressive loading at a constant displacement rate of 0.5 mm/min. A spherically-seated compression tool (3 1/8 inch diameter) is suspended from the crosshead of the machine to compensate for possible non-parallel bearing surfaces of a specimen being tested. The ultimate load necessary to break a specimen is indicated by the machine.

J. Permeameter

1. A holder will be provided to receive the modified nipple mold that contains the specimen to be tested.

2. A pair of capacitance-sensing, pressure transducers of 17-4PH stainless steel will be used to measure [with an imprecision of about 3 kPa (0.4 psi)] the pressure difference that is applied to opposite sides of a specimen which is under an ambient pressure up to 60 MPa (8,700 psi).

3. A recording potentiometer will be used to measure the net output of these pressure transducers (14 kPa/mV). The exponential decay of this output is related to the permeability of the specimen being tested (See Section VI A).

K. Pressure Transmitter

It is planned tentatively to use a stainless steel bellows to transmit an applied pressure to one end of a steel rod so that the shear-bond strength of the steel-cement interface can be measured at elevated temperature and pressure.

IV. Preparation of Specimens

A. Slurry Mixing

The API recommended practice (section 3 of reference 2) will generally be followed unless otherwise directed by the supplier. In brief, a weighed quantity of distilled water which is required to prepare one liter of slurry will be placed in the mixing container, the mixer turned on the slow speed, and the weighed quantities of dry components added in less than 15 s. Next, the cover will be placed on the container, and stirring will be continued at the high speed for 40 s.

B. Molding

1. Prior to mixing a slurry of a given cementing material, silicone grease will be thinly applied to the inside surfaces of ten Pyrex tube molds. Also, seven modified nipple molds of stainless steel and five

steel rods will be washed with trichloroethylene. These molds will provide all the specimens that are needed for the series of property tests which will be conducted at room temperature and pressure on a given cementing material.

2. The slurry of a cementing material which is prepared according to section IV A will be poured into these molds and puddled as needed to remove air bubbles. Five of the modified nipple molds will enclose centered steel rods. The excess slurry in the modified nipple molds will be struck off even. The molds will be appropriately covered as indicated in section III C, submerged upright in distilled water at 25 °C, and sealed in the stirred autoclave.

C. Set-Curing

1. The set-cure will commence at the application of pressure and temperature. First, the autoclave will be partially pressurized with nitrogen or argon; then it will be automatically heated from room temperature to 200 °C in about 75 min., the temperature rate being fairly constant at 3 °C/min during the first 60 min. The contents of the autoclave will be maintained at 200 °C for the remainder of the cure. The quantity of distilled water and the initial pressure of nitrogen are chosen such that the volume ratio of the final gas phase to vessel capacity is about ten percent and the final pressure will be near, but eventually adjusted to 20 MPa (2900 psi) when the operating temperature is attained.

2. When the set-curing has progressed 48 h, the heating will be terminated and water-cooling through an internal coil of the autoclave will begin to reduce the temperature at a fairly constant rate, ultimately to 60 °C in 45 min; then the pressure in the autoclave will be gradually released.

D. Finishing Operations

1. At the conclusion of a set-cure the Pyrex molds of set cement will be removed from the stirred autoclave, and the Pyrex tubes will be broken away by diamond scribing the tubes and gentle tapping.

2. Each of the ten rods of set cement will be sawed perpendicular to its longitudinal axis into three specimens which are twice as long as their diameter. These pieces will be identified as the top, middle, and bottom of a given rod.

3. The seven modified nipple molds of set cement will be removed from the stirred autoclave, and their cover plates and Teflon sheets detached. If the surfaces of the set cement are glazed they will be scraped lightly with a wire brush under a stream of water to remove such glaze.

4. The finished specimens resulting from a set-cure will be submerged in water in a constant temperature bath at 25 °C for storing until some specimens are property tested and the remainder are exposed to simulated geothermal fluids. A weekly schedule which includes specimen preparation is indicated in Table I.

V. Exposures in Simulated Geothermal Fluids

A. Fluid Compositions

Two aqueous solutions of different concentrations of certain salts and carbon dioxide will be used to represent light and heavy geothermal fluids, respectively. Appropriate quantities of NaCl, KCl, CaCl_2 , and NaHCO_3 will be weighed and dissolved in distilled water to provide the compositions which are shown in Table II. When the solutions A and B are placed in their respective reservoirs, carbon dioxide gas at given partial pressures will be bubbled through the solutions at 25 °C until

they are equilibrated at pH values of 5.5 and 5.0, respectively, Thereafter, these partial pressures of CO₂ will be maintained in the respective reservoirs, also in the Hastelloy pressure vessels while they are at 25 °C. [Note: The compositions of solutions A and B were arbitrarily selected. As reference 5 indicates, geothermal fluids from various locations differ considerably in composition; moreover, the analyses at a given site show varying results. The composition of solution A corresponds to the average of the principal components in 14 analyses of the East Mesa 6-1 wellhead fluid which was collected in the spring of 1977 (reference 6). The analyses of the Salton Sea fluids which are reported in reference 5 served as guidelines in the selection of the composition of solution B. The exposure temperatures given in Table 2 are consistent with the corresponding Na/K mass ratios, which are used to indicate bottom hole temperatures (reference 9). The exposure pressures of solutions A and B correspond to well depths of about 2200 and 1500 m, respectively.]

B. Temperature and Pressure Conditioning

1. The four Hastelloy pressure vessels will be divided evenly to contain the two solutions A and B and will be operated at the temperatures and pressures which are specified in Table II for these respective solutions.

2. In regard to the exposures of specimens which will be property tested at 25 °C, the Hastelloy pressure vessels will be pressurized and heated in a manner similar to that which is described in section IV C for the stirred autoclave. The quantities of exposure solutions which are added to the vessels containing the specimens at room temperature are chosen such that the volume ratio of final gas phase to vessel capacity is about ten percent when the operating temperature is attained. Also, nitrogen or argon will be added to the contents of these vessels

at room temperature such that the respective final pressures will be near, but eventually adjusted to the values given in Table II. Once a week the vessels will be appropriately cooled and dismantled. Table I gives a weekly schedule for these operations.

C. Scheduling of Set Cements

1. Specimens of a given set cement will commence being exposed unprotected in the two solutions A and B about 27 and 51 h, respectively, after the conclusion of their set-cure.

2. Eight rods of three sawed specimens each, which are designated for the compressive and tensile strength tests, will be divided evenly and deposited at the appropriate times in two Hastelloy pressure vessels, holding solutions A and B, respectively. Teflon sheets or stainless steel shims (0.05 mm thickness) will be used to separate the sawed ends of these specimens to keep them from sticking together while they are stacked in the vessels during the exposures. Half of these specimens will be exposed one week and the other half, exposed four weeks. Table III shows a schedule of depositing and withdrawing this type of specimen for several set cements in a particular solution.

3. Likewise, the four specimens which are designated for the shear-bond strength test and the two specimens which are designated for the permeability test will be divided evenly and deposited in the other two Hastelloy pressure vessels, holding solutions A and B, respectively. Half of the shear-bond specimens will be exposed one week and the other half, exposed four weeks; the same permeability specimens will be used throughout. Table IV shows a schedule of depositing and withdrawing these types of specimens for several set cements in a particular solution.

VI. Property Tests

A. Permeability of Set Cement

1. The measurement technique to be employed for determining permeability is a pulsed technique, similar to that described in reference 10, except that the range of conditions has been extended so that measurements can be made both at room temperature and atmospheric pressure and at elevated pressure and temperature, using the Hastelloy pressure vessels.

2. A mold with its set-cured specimen is sealed in a test holder, using Teflon tape. The holder is filled with the fluid that was used in the set-cure or in the particular exposure that this test follows. When the ambient temperature and pressure are established on both sides of the specimen, a vent valve on the holder is opened momentarily to allow fluid from the fluid reservoir to be pumped through the holder until any air in the holder is displaced.

3. A differential pressure of 2.0 MPa (290 psi) is applied across the specimen of set cement to establish the fluid flow through the cement. The fluid in the holder is then isolated from its reservoir, and the decline of the pressure difference is recorded as a function of time.

4. The fluid permeability (k) of the set cement is calculated from the observed logarithmic slope

$$d \ln (P_1 - P_2) / dt = -k A (1/V_1 + 1/V_2) / \mu \beta L$$

where

P_1 = pressure of fluid in holder,

P_2 = ambient pressure downstream,

t = time,

A = cross-sectional area of specimen,

L = length of specimen,
 μ = fluid viscosity,
 β = fluid compressibility,
 V_1 = volume of fluid in holder, and
 V_2 = ambient volume downstream.

[Note: When measurements are made at room temperature and pressure, P_2 remains constant and $1/V_2$ is assumed zero.]

B. Shear-Bond Strength of Cement-Steel Interface

1. We plan to conduct this test at room temperature and pressure and also at elevated temperature and pressure, using the Hastelloy pressure vessels.

2. A mold containing a cement specimen with a centrally embedded steel rod is supported in a test holder, and a load is applied to the end of the steel rod which is in the larger opening of the mold. The maximum force (F) required to displace the steel rod is recorded and used to calculate the shear-bond strength.

3. The shear-bond strength (s) is calculated from

$$s = F/\pi DL$$

where

F = maximum force required to displace the steel rod,

D = diameter of steel rod, and

L = length of the cement-steel rod interface.

[Note: The shear-bond strength determined at room temperature can be reduced from its actual value when the thermal expansion of the set-cured cement is less than that of the steel; on the other hand the mold-cement interface might fracture first during a test, despite its larger diameter, if the relative thermal expansion difference is reversed.]

C. Compressive Strength of Set Cement

1. The testing procedure will generally be in accordance with ASTM Standard Method C-39 (reference 11) except that the specimen dimensions are smaller than those customarily used. The bearing block faces and the test specimens are wiped clean, and the specimen is centered directly under the spherically seated upper bearing block that is able to rotate freely. The universal testing machine will apply a compression load at a constant displacement rate of 0.5 mm/min until the maximum force necessary to fracture the specimen is recorded.

2. The compressive strength (S_c) is calculated from

$$S_c = 4F/\pi D^2$$

where F = fracture force applied to the face of the set cement and
 D = diameter of set cement.

D. Tensile Strength of Set Cement

1. The testing procedure will generally be in accordance with ASTM Standard Method C496 (reference 12) except that the specimen dimensions are smaller than those customarily used. Unused strips of cardboard (0.5 mm thick) are used as cushions between the specimen and the load bearing surfaces to distribute the load smoothly. Using marked diametral lines, the specimen is centered on its side between the bearing blocks. The testing machine is used to apply diametral compression loading at a constant displacement rate of 0.5 mm/min until the maximum force required to fracture the specimen is indicated by the machine.

2. The tensile strength (S_t) is calculated from

$$S_t = 2F/\pi DL$$

where F = fracture force applied along length of specimen,
 D = diameter of specimen, and
 L = length of specimen.

E. Tests at Room Temperature and Atmospheric Pressure

1. The property tests listed above will be conducted on moist specimens after the set-cure and after one and four week exposures to the simulated geothermal fluids. Specimens will be stored in the 25 °C constant temperature bath prior to their property testing. As Table I indicates, the property tests will commence approximately four hours after the set-cure has been terminated and approximately 2 1/2 h after the exposures in solutions A and B.

2. The two permeability specimens for a given set cement will be used in the tests which follow a set-cure; and then these same specimens will be used again after their respective exposures in solutions A and B.

3. Only one shear-bond strength specimen will be tested following each set cure or exposure condition.

4. Three specimens sawed from a rod of a given set cement will be used each time that either a compressive strength test or a tensile strength test is conducted. Tables III and IV indicate the order of weeks when the specimens of the various set cements are removed from their exposures in either of the two simulated geothermal fluids. We plan to duplicate this series of tests at a later time.

F. Tests at Elevated Temperatures and Pressures

When the first series of tests at room temperature and atmospheric pressure are concluded, permeability and shear-bond strength test will be conducted at elevated pressure and temperature. Priority for selection of cements for these *in situ* tests will be based on the ranking of materials from the tests at room temperature and atmospheric pressure. Alternate *in situ* property tests are also being considered (for example, shear-bond strength to rock, tensile-bond strength to steel and to rock, and biaxial flexural strength), but we do not presently plan to conduct these tests on all of the candidate cementing materials.

Table I. Weekly schedule of specimen preparation, exposures, and room temperature property testing.

Day	Time	Operation
Monday	8:30 am	Prepare slurry and fill molds.
	10:30 am	Assemble stirred autoclave.
	11:00 am	Commence set-curing.
	1:00 pm	Prepare simulated geothermal fluids.
Tuesday	8:30 am	Calculate results of previous week and prepare report.
Wednesday	11:00 am	Terminate set-curing.
	12:00 noon	Dismantle stirred autoclave.
	12:30 pm	Remove molds from specimens.
	1:30 pm	Saw specimens.
	3:00 pm	Conduct permeability tests on set-cured specimens.
	4:30 pm	Conduct load tests on set-cured specimens.
Thursday	8:30 am	Terminate exposure of specimens in first fluid.
	10:00 am	Dismantle two pressure vessels holding first fluid.
	11:00 am	Conduct permeability tests on exposed specimens.
	1:30 pm	Assemble two pressure vessels holding first fluid.
	2:00 pm	Commence resumption of exposure of specimens in first fluid.
	4:00 pm	Conduct load tests on exposed specimens.
Friday	8:30 am	Repeat Thursday schedule for specimens in second fluid.

Table II. Temperature, pressure, and composition of solutions ^a to be used for exposure of set-cements.

	Units	Solution A	Solution B
T	°C	190	320
P(total)	MPa (psi)	20 (2900)	13 (1900)
P(CO ₂), 25°C	MPa (psi)	0.04 (6) ^b	0.4 (60) ^b
pH, 25°C		5.5	5.0
NaCl	mol/kg	0.31	2.3
KCl	mol/kg	0.019	0.36
CaCl ₂	mol/kg	0.020	0.66
NaHCO ₃	mol/kg	0.0015	0.0035
Density, 25°C	g/ml	1.01	1.16
Total dissolved solids	mass per cent	2	20

^aThe solutions A and B simulate light and heavy geothermal fluids, which are representative of the East Mesa 6-1 and Salton Sea areas, respectively (reference 6 and 5).

^bThese values are estimates based on data for ideal solutions from reference 7 and corrected by data for the salting out effect from reference 8.

Table III. Schedule of exposing compressive and tensile specimens of set cements in a simulated geothermal fluid at an elevated temperature and pressure.

Week	Cement	Specimens		Balance
		Deposited	Withdrawn	
0	a	12a		12
1	b	12b	6a	18
2	c	12c	6b	24
3			6c	18
4	d	12d	6a	24
5	e	12e	6b, 6d	24
6	f	12f	6c, 6e	24
7			6f	18
8			6d	12
9			6e	6
10			6f	0

Table IV. Schedule of exposing shear-bond (s) and permeability (p) specimens of set cements in a simulated geothermal fluid at an elevated temperature and pressure.

Week	Cement	Specimens			Balance
		Deposited	Withdrawn	Re-deposited	
0	a	2s _a , p _a			3
1	b	2s _b , p _b	s _a , p _a	p _a	5
2	c	2s _c , p _c	s _b , p _b	p _c	7
3			s _c , p _c	p _c	6
4	d	2s _d , p _d	s _a , p _a		7
5	e	2s _e , p _e	s _b , s _d , p _b , p _d	p _d	7
6	f	2s _f , p _f	s _c , s _e , p _c , p _e	p _e	7
7			s _f , p _f	p _f	6
8			s _d , p _d		4
9			s _e , p _e		2
10			s _f , p _f		0

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