CEMENTING OF GEOTHERMAL WELLS

PROGRESS REPORT NO. 7
OCTOBER - DECEMBER 1977

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Abstract

A coordinated program for the development of improved cements specifically designed for geothermal well applications was started in April 1976. Since that time an assessment of the state of the art of well cementing has been made, a management plan prepared, and research on organic and inorganic cementing materials started. Work accomplished during the period October 1 - December 31, 1977 is described in the current report.

Summary

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

Work on the first element of the program management plan (problem definition) has been completed by Dowell and a report issued. The materials development and property verification phases of the plan are in progress. Plans for the down-hole testing phase of the program are being formulated. The Geothermal Well Cementing Advisory Panel has been affiliated as a Task Group of the American Petroleum Institute's Committee on Standardization of Oil Well Cements

The most promising high temperature polymer cement system identified to date consists of a cross-linked mixture of styrene, acrylonitrile, and acrylamide in conjunction with a sand-cement filler. A study is in progress to optimize the concentrations of the mix components with respect to properties. Work to determine the pumpability of the system is in progress.

Samples of PC have been removed after exposure at The Geysers to dry steam at 460°F (238°C) for 2 yrs. Visual inspection of the specimens indicated little apparent deterioration.

Cementing of Geothermal Wells

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Introduction

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

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

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

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

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

The goals for the overall program are as follows:

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

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

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

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

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

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

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

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

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

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

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

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

This report constitutes the seventh in a series of quarterly reports describing work on the program. Accomplishments during the period October-December 1977 are summarized below. During the quarter work has been performed in Tasks 1, 2, 3, and 7. Work on other tasks will commence as the research work progresses.

Task 1. Program Management Plan

The need for DOE to sponsor a program to develop improved geothermal cementing materials was ascertained by evaluating information obtained from well owners, cementing service companies, and governmental and private research organizations. The consensus of those contacted was that the program should be a cooperative one performed on a cost-sharing basis with well cementing service companies and well owners. It was also established that the focal point of the program should be a series of downhole test facilities. Testing should be performed in several geothermal environments but the highest priority for near-term (~ 10 yr) application

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

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

Problem definition, Dowell Division of Dow Chemical Co.

Materials development, Battelle's Columbus Laboratories

Brookhaven National Laboratory

Colorado School of Mines

Dowell Division of Dow Chemical Co.

Pennsylvania State University

Southwest Research Institute

University of Rhode Island

Property verification, National Bureau of Standards

As a means of obtaining technical guidance for the overall program and as an initial step in the technology transfer process, BNL has established a "Geothermal Well Cement Advisory Panel". The panel has recently been affiliated as a Task Group of the American Petroleum Institute's (API) Committee on Standardization of Oil Well Cements.

Mr. J.P. Gallus of Union Oil of California will serve as the chairman of the Task Group. Current members are listed below.

L.E. Kukacka, BNL, Panel Chairman

J.P. Gallus, Union Oil of California, Task Group Chairman

L.E. Baker, Sandia Laboratories

D. Free, Dowell

C.E. Johnson, Chevron Oil Field Research Company

G.L. Kalousek, Colorado School of Mines

S. Maravilla, Universal Atlas Cement Company

R.R. Reeber, Division of Geothermal Energy, DOE

F. Shell, Phillips Petroleum Company

D.K. Smith, Halliburton Services

S.M. Weiderhorn, National Bureau of Standards

The second meeting of the panel was held at the Union Oil of California Research Center in Brea, California on December 7, 1977. All subcontractors made presentations at the meeting.

At the conclusion of the technical presentations, the Advisory Panel members discussed the current status of geothermal well completion systems and the contributions that the current DGE program will make. The consensus of the panel was as follows:

1. The consequences from a geothermal well blowout may be much worse than from an oil well due to the large quantity of high temperature fluid that will be released. A current blowout in Iceland which has been out of control for several months was cited as an example.

2. Geothermal wells differ from oil wells in that they do not utilize a production string, production packer, and a subsurface safety

valve. Also, the geothermal fluid is in direct contact with the casing. Therefore, greater reliability in components such as the casing and cement is needed. Improved cements will reduce the probability of well failures and will have significant effects on the economic and environmental aspects of geothermal energy.

3. Standards are needed for geothermal cements used in hydrothermal, steam, and geopressure wells. API standards on oil well cements only go to 200°C (392°F).

4. The need to obtain long-term data on cementing systems was emphasized. Life expectancy data could be used in determining when a well should be shut down before a failure occurs. These data can best be obtained in down-hole tests and in demonstration wells.

5. Due to the larger number of water-dominated reservoirs, durability of the cements to brine should have a higher priority than steam.

6. Good technical progress in the DGE program was apparent. The program is broad-based with a minimum of duplication. The probability of attaining the goals of the program appears high. The minimum return from the program will be a better understanding of how the currently used cements react in geothermal environments. This will lead to standards. These data will also be of value in obtaining drilling permits and in predicting when well problems may occur.

Task 2. Selection of Well Cementing Materials

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

Polymer Cements

Polymer cements (PC) have been identified as promising well completion materials. During the current report period several monomer systems have been evaluated. These are listed in Table 1.

Sample Preparation

Earlier work² has indicated that a silica sand mixture consisting of 50 parts by weight of sieve size No. 16, 25 parts of No. 30, and 25 parts of No. 100 has the proper particle size distribution to produce a high quality PC with a minimum polymer content. For high temperature applications, Type III portland cement is added to this mixture to enhance the durability to brine and steam. Possible explanations for this effect were discussed in the previous report.³

The monomers are mixed in a glass beaker and polymerization initiator is added and dissolved. If acrylamide or methacrylamide are included in the monomer mixture, the mixture is heated to 122°F (50°C) prior to the addition of initiator to dissolve the solid monomer. The formulation is mixed with the sand-cement aggregate and placed in a glass tube which is coated with a release agent. Vibration is used to compact the PC. The samples are cured in an oven at 140°F (60°C) for 16 hr and for 2 hr at 185°F (85°C). After cooling, the samples are removed from the form. Prior to testing, they are cut to a length to diameter ratio of 2, and dried for 18 hr at 220°F (105°C).

Copolymer Systems

Several monomer mixtures have been used to produce high temperature PC formulations. The properties of these materials are summarized in Tables 2 and 3. It can be seen from the tables that formulations

TABLE 1

Properties of Monomer Systems for High Temperature PC Applications

<u>Monomer</u>	<u>Structure</u>	<u>Molecular weight</u>	<u>Melting point, °C</u>	<u>Boiling point, °C</u>	<u>Flash point, °C</u>	<u>Condition</u>
styrene (St)	$C_6H_5CHCH_2$	104.14	-31	146	31.1	liquid
acrylonitrile (ACN)	CH_2CHCN	53.06	-82	77.3	1.1	liquid
acrylamide (Aa)	$CH_2CHCONH_2$	71.08	84.5	125	—	solid
methacrylamide (MAa)	$CH_2CHCONHCH_3$	85.1	111	—	—	solid
isobornyl methacrylate (IBOMA)	$C_{10}H_{17}OOC\overset{\overset{CH_3}{ }}{C}CH_2$	222	—	—	127.7	liquid
ethylthioethyl methacrylate (ETEMA)	$C_2H_5SC_2H_4OOC\overset{\overset{CH_3}{ }}{C}CH_2$	174	—	102	79.4	liquid
methyl methacrylate (MMA)	$CH_3CCHCOOCH_3$	100.1	-50	101	0	liquid

TABLE 2

Polymer Concrete Properties

Monomer system	Monomer ratio	Polymer weight loss after 30 days at 460°F	Boiling Water absorption, %, after			Compressive strength, psi, after			
			prep.	32 days in oven at 460°F	autoclave	prep.	boiling water absorp.	32 days in oven at 460°F	autoclave
St-ACN-Aa	57.5-40-2.5	18.0	2.27	5.09	1.71	20542	10542	3111	10942
	60-35-5.0	25.6	1.37	6.66	2.0	24375	19750	2013	12030
	55-40-5.0	18.8	0.98	4.73	1.84	19750	20167	7128	13547
	55-37.5-7.5	28.5	0.96	10.03	1.38	20917	21083	752	5812
St-ACN-MAa	57.5-40-2.5	25.5	2.74	6.80	3.59	15333	13000	1812	5919
	60-35-5	18.4	1.88	4.84	2.64	17042	13458	3111	10855
	55-40-5	15.8	1.49	5.43	1.30	19000	19167	5396	7222
	55-37.5-7.5	9.6	0.94	2.57	1.55	22250	14833	5496	8889

1. monomer loading - 12 wt%
2. sand-cement ratio, 80-20
3. initiator, azobisisobutironitrile (AIBN)

TABLE 3
Polymer Concrete Properties

Monomer system	Monomer ratio	Catalyst		Boiling water absorption, %,	Boiling water absorption, %, after oven at 460°F	Weight loss after oven at 460°F	Compressive strength, psi, after			Boiling water absorp. after autoclave %
		name	wt%				prep.	Boiling water absorp.	autoclave	
IBOMA-MMA 12% monomer loading	95-5	BPO	2.0	0.16	22.70 ¹	7.98 ¹	10442	13009	4008	3.51
	90-10	AIBN	0.75	0.34	15.47	8.79	12279	13208	6723	3.71
	85-15	AIBN	0.75	0.38	17.83	8.76	11504	11482	5824	4.45
	80-20	BPO	2.0	0.16	17.98	8.51	15443	15730	7513	2.70
	70-30	AIBN	0.75	0.50	13.84	8.02	14049	13363	7644	3.64
	60-40	AIBN	0.75	0.57	14.32	8.31	14226	11062	10235	3.38
	50-50	BPO	2.0	0.37	15.46	7.71	20957	19956	13135	1.66
IBOMA-MMA -ETEMA 13% monomer loading	94-5-1	AIBN	0.75	0.54	19.33 ²	8.59 ²	10363	9615	6899	5.22
	84-15-1	AIBN	0.75	0.64	19.75	7.78	13184	11880	5025	5.28
	69-30-1	AIBN	0.75	1.05		7.37	13931	10748	7000	3.92
	59-40-1	AIBN	0.75	1.19	20.55	7.72	14744	7927	6798	3.69
	49-50-1	AIBN	0.75	1.48	18.09	7.76	15214	9103	6378	4.68
	90-5-5	AIBN	0.75	0.56	25.39	8.41	12799	8953	5168	5.10
	80-15-5	AIBN	0.75	0.85	18.81	7.49	14385	10855	4748	5.85
	70-25-5	AIBN	0.75	1.20	18.89	6.21	9145	8718	4983	5.69
	70-20-10	AIBN	0.75	0.64	19.11	6.73	14359	12222	6143	4.53
	60-30-10	AIBN	0.75	1.12	16.64	6.49	16047	12777	6487	4.52
	50-40-10	AIBN	0.75	0.78	18.95	6.73	17308	16803	9211	3.47

1, after 1 day exposure at 460°F

2, after 4 day exposure at 460°F

containing styrene (St) - acrylonitrile (ACN) - acrylamide (Aa) and St - ACN - methacrylamide (MAa) produce PC with properties superior to those containing isobornyl methacrylate (IBOMA), ethylthioethyl methacrylate (ETEMA) and methyl methacrylate (MMA). As a result, emphasis has been placed on the development of the first two systems.

Experiments were performed to determine if copolymers or mixtures of homopolymers of St, ACN, Aa or MAa were formed during the polymerization process. The formation of copolymers was confirmed by solubility tests. It was determined that the copolymerization products do not dissolve in solvents for polyacrylonitrile such as dimethylformamide or in acetone, a solvent for polystyrene. This indicates the absence of homopolymers. It was also noted that homogeneous transparent films without signs of inclusions were produced when the copolymers were press-molded. This also is evidence of the formation of true copolymers.

An IR spectroscopy investigation of the molecular structure of the copolymerization products (Figure 1) showed that all absorption bands characteristic of polystyrene, polyacrylonitrile, and polyacrylamide (3400-3500, 3040, 2930, 2220, 1600, 1500, and 1450 cm^{-1}) are present in the spectra.

Tests have been performed to optimize the monomer composition with respect to the properties of the PC. The concentrations of each monomer constituent in the formulations were selected based upon the reactivity of each monomer. PC samples were made containing 12 wt% of the monomer formulations and 88 wt% of filler composed of an 80-20 silica sand - Type III portland cement mixture. The results from property evaluations performed on these specimens are given in Table 2. These data indicate that the boiling water absorption after exposure of the specimens in an

Figure 1. Infra-red structure of St-ACN-Aa copolymer.

oven at 460°F (238°C) for 32 days increases as the concentration of Aa is increased and decreases with increased MAa content. These data are plotted in Figure 2. The compressive strength increases with increased MAa and decreases as the Aa concentration is increased (Figure 3).

The addition of cross-linking agents to the monomer mixtures improves the thermal and chemical stability of the copolymers. Two cross-linking materials, trimethylolpropane trimethacrylate (TMPTMA) and divinyl benzene (DVB), are being studied. Data from these studies are given in Tables 4 and 5 and Figures 4-6. These results indicate that the optimum TMPTMA concentration as determined by compressive strength (Figure 4), boiling water absorption (Figure 5), and weight loss tests is between 5 and 7 wt%.

Studies to determine the effect of the ratio of ACN to St in formulations containing St - ACN - Aa and a crosslinking agent (TMPTMA or DVB) were also performed. Data plotted in Figure 7 indicate that for a TMPTMA concentration of 5 wt%, the compressive strengths of PC samples after exposure to air at 460°F (238°C) and to brine at 460°F (238°C) are essentially the same. The strength is maximum in the ACN/St range of 0.4 to 0.5 and then decreases. This is in good agreement with copolymerization theory.

The effect of DVB concentration on the properties of PC containing St - ACN - Aa was determined. The data indicate that the optimum concentration is in the range 1 to 8 wt%. In this range, the PC has the highest compressive strength (Figure 8), lowest water absorption (Figure 9), and lowest weight loss after exposure to hot air (Figure 6). Increasing ACN/St ratios in the range 0.45 to 0.8 in PC samples containing 1 wt% DVB (Figure 10) increases the initial compressive strength from ~12,000 to 17,000 psi.

Figure 2. The effect of monomer composition on the boiling water absorption of PC.

Figure 3. The effect of monomer composition on the compressive strength of PC. 1, 1¹, St - ACN - Aa; 2, 2¹, St - ACN - MAa.

TABLE 4

Concentration of TMPTMA as a Function of Properties of Polymer Concrete

Concentration TMPTMA, wt%	ACN St ratio	Compressive strength, psi., after				Polymer weight loss after 30 days in oven at 460°F, %	Boiling water absorption after	
		prep.	boiling water absorption	oven, 30 days at 460°F	autoclave 460°F		autoclave, %	oven, %
0	0.73	19750	20167	7128	13547	18.8	2.00	6.66
	0.60	24375	19750	2013	12030	25.6	1.71	5.09
2.5	0.64	22832	23009	9217	15420	10.0	0.83	1.71
5.0	0.80	26842	25000	11200	12435	5.96	0.71	0.65
	0.64	25817	26754	17409	16000	5.94	0.70	0.52
	0.50	27895	26316	20348	20348	5.96	0.68	0.61
	0.38	26053	23421	20522	19304	7.96	0.71	0.85
7.5	0.82	27982	27193	22000	8000	5.06	0.59	0.35
	0.66	23333	21491	21739	8087	5.03	0.71	0.46
	0.52	20965	16404	22696	5044	5.41	0.51	0.50
	0.40	29737	17895	24087	12870	6.19	0.53	0.63
10	0.88	28597	27281	12226	5130	7.09	0.69	0.64
	0.69	28158	26053	16696	11304	5.16	0.63	0.40
	0.55	26930	23509	25478	11913	5.89	0.62	0.64
	0.42	26404	18333	25130	13148	5.44	0.43	0.48

Acrylamide concentration, 5 wt%

TABLE 5

Concentration of DVB as a Function of Properties of Polymer Concrete								
Concentration DVB, wt%	ACN St ratio	Compressive strength, psi., after				Weight loss of polymer after 30 days in oven at 460°F, %	Boiling water absorption after	
		prep.	boiling water absorption	oven, 30 days at 460°F	autoclave 460°F		autoclave, %	oven, %
Concentration Aa, 5 wt%								
0	0.73	19750	20167	7128	13547	18.8	2.00	6.66
	0.76	24375	19750	2013	12030	25.6	1.71	5.09
1.00	0.74	24825	25263	16870	18435	6.12	1.03	0.71
	0.59	25263	22632	16609	16696	5.86	0.78	0.61
	0.47	21754	18947	11652	21913	7.19	0.63	0.88
-17- 2.5	0.85	28070	26930	18365	13826	5.48	0.73	0.56
		26496	25043	19159	22393			
	0.76	24211	23622	17878	22348	5.62	0.60	0.60
	0.60	24737	22895	16783	13304	5.54	0.64	0.53
	0.48	25351	22018	21670	22609	5.44	0.69	0.67
5.0	0.80	25128	23675	16965	27607	6.76	0.69	1.14
7.5	0.75	22906	23504	14310	29915	8.30	0.58	1.61
10	0.70	21966	23162	7761	27778	12.89	0.52	2.76
Concentration MAa, 5 wt%								
2.5	0.85	26552	26000	17148	20128	4.83	0.65	0.58
5.0	0.80	25130	24000	18383	16068	4.84	0.48	0.69
7.5	0.75	22348	23913	14835	8761	4.44	0.59	0.51
10.0	0.70	18522	18957	19300	17992	14.13	4.13	0.60

Figure 4. Compressive strength as a function of crosslinking agent concentration.

Figure 5. The boiling water absorption of PC as a function of TMPTMA concentration.

Figure 6. Polymer weight loss as a function of crosslinking agent concentration.

Figure 7. The compressive strength of PC containing TMPTMA as a function of ACN/St ratio.

NOTE: CONCENTRATION $A_0 = 5\%$ BY WEIGHT

Figure 8. The compressive strength of PC as a function of DVB concentration.

Figure 9. The boiling water absorption of PC as a function of DVB concentration.

Figure 10. The compressive strength of PC containing DVB as a function of ACN/St ratio.

Additional work is in progress to determine which of the two cross-linking agents is superior. At this time samples containing DVB appear more stable to hot brine than samples containing TMPTMA. In hot air, the opposite trend has been observed.

Another important parameter in the preparation of PC is the effect of polymer content on the properties of the composite. To obtain information on this variable, a series of PC samples containing a monomer mixture of 55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA in conjunction with a 70 wt% silica sand - 30 wt% Type III portland cement aggregate were tested. The polymer loading was varied between 12 and 20 wt%. These results, summarized in Table 6 and Figure 11, indicate that the compressive strengths decreased with increasing polymer loading.

If a PC containing 12 wt% polymer can be assumed to be a homogeneous system, further increases in polymer content results in the formation of heterogeneous sections of polymer. These impede the filling of the capillaries, therefore reducing the cohesive force between polymer and aggregate. Electron microscopic studies support this assumption. Figures 12-13 show fractured surfaces of PC samples containing 12 and 20% polymer loadings, respectively. The composite containing 12 wt% polymer (Figure 12) has a more uniform surface than the sample containing 20 wt% (Figure 13). The polymer appears to be evenly filling the pore space between the sand grains and cement and a continuous three-dimensional polymeric network is formed.

Studies are also in progress to determine the optimum ratio of sand to cement in the aggregate used to produce PC. The results from these studies

TABLE 6

Summary of Test Results for Polymer Concrete Systems Containing
55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA and 70 wt% - 30 wt% Sand-Cement Aggregate

Property	Monomer loading, wt%			
	12.0	15.0	17.5	20.0
Compressive strength (psi) after				
a. preparation ¹	28319	25421	24737	17457
b. boiling water	25841	23333	22193	21053
c. oven (30 days, 460°F)	17537	12649	14297	11955
d. autoclave (10 days, hot brine)	17743	16052	15704	
Boiling Water absorption (%) after				
a. preparation ¹	0.33	0.26	0.26	0.24
b. oven (30 days, 460°F)	0.90	1.10	1.27	1.47
c. (10 days, hot brine)	0.64	0.64	0.59	

1. average of 4 specimens

Figure 11. The effect of polymer loading on the compressive strength of PC.

Figure 12. Scanning electron microscope picture of fractured surface of PC sample containing a 12% polymer loading.

Figure 13. . Scanning electron microscope picture of fractured surface of PC sample containing a 20% polymer loading.

are summarized in Table 7 and Figure 14. It was observed that increases in cement content from 10 to 30% resulted in increases in compressive strength from 20,000 to 27,000 psi. The water absorption remained essentially constant over this range. Further increases in cement content reduces the strength and increases the water absorption. This may be explained by the reduced porosity resulting from the added cement fines. This reduces the cohesive forces between the polymer and the filler. As discussed above, increases in the polymer content of the mix beyond 12 wt% results in further reductions in properties.

Based upon the results to date, the optimum filler composition for use with the St - ACN - Aa - TMPTMA system is in the range 70 to 80 wt% silica sand and 20 to 30 wt% cement.

During the next report period the following work will be performed.

1. The thermal properties of the systems as a function of ACN concentration will be determined.
2. Long-term laboratory and field tests to determine the durability will be continued.
3. Tests to determine the pumpability of the systems will be initiated. The design of equipment to perform this work has already been started.
4. Experiments using siloxane as a high temperature binder for PC will be initiated.

TABLE 7

Properties of Polymer Concrete as a Function of Sand-Cement Composition

Aggregate composition, sand-cement, wt%	90-10	80-20	70-30	60-40	50-50
Monomer composition	55 wt% St - 35 wt% ACN - 5 wt% Aa - 5 wt% TMPTMA				
Boiling water absorption (%) after:					
a. preparation	0.78	0.62	0.85	0.38	0.42
b. oven (30 days, 460°F)	0.90	1.02	0.87	1.18	2.69
Compressive strength (psi) after:					
a. preparation	22212	24248	28319	20620	26549
b. boiling water	20266		27841	22920	23028
c. oven (30 days, 460°F)	18926	15537	17547	19174	16694
Monomer composition,	55 wt% St - 37.5 wt% ACN - 7.5 wt% MAa				
Boiling water absorption (%) after:					
a. preparation	2.05	1.25	1.41	2.33	2.63
b. oven (30 days, 460°F)	5.57	3.82	4.06	7.21	7.42
Compressive strength (psi) after:					
a. preparation	14655	15080	18620	13327	7168
b. boiling water	10779	19097	15027	6478	5699
c. oven (30 days, 460°F)	3652	4300	2209	1565	973

Figure 14. The effect of sand-cement content in aggregate on the properties of PC:

Inorganic Cements

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

Colorado School of Mines

G.L. Kalousek, Principal Investigator

Starting date, April 1977

Status; The second quarterly report for the program was included with Report No. 6³. The third report has not yet been received.

University of Rhode Island

T.J. Rockett, Principal Investigator

Starting date, July 1977

Status; The second quarterly report for the program is given in Appendix 1.

Dowell Division of Dow Chemical

B.E. Simpson, Principal Investigator

Starting date, July 1977

Status; A Phase I report summarizing the state of the art of well cementing and progress made during July-December 1977 has been issued and is given in Appendix 2.

Battelle's Columbus Laboratories

R.S. Kalyoncu, Principal Investigator

Starting date, September 1977

Status; The first quarterly report for the program is given in Appendix 3.

Pennsylvania State University

D.M. Roy, Principal Investigator

Starting date, September 1977

Status; The first quarterly report for the program is given in Appendix 4.

Southwest Research Institute

D.K. Curtice, Principal Investigator

Starting date, October 1977

Status; The first quarterly report for the program is given in Appendix 5.

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

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

Samples of polymer cement containing 50 wt% St - 33 wt% ACN - 17 wt% TMPTMA and 55 wt% St - 36 wt% ACN - 9 wt% TMPTMA have been removed from a well-head test chamber at the Geysers after exposure to dry steam at 460°F (238°C) for 2 years. Visual inspection of the materials indicated them to be in good condition. Strength tests are currently being made.

A testing program that will be a precursor to down-hole evaluation is in progress at the National Bureau of Standards. Test procedures have been developed and equipment assembled. Samples of oil well cements used for the completion of geothermal wells are in test. A progress report for this program has not yet been received.

Task 7. Administrative

During the current report period, three "Monthly Administrative Letters" were submitted to DGE and Quarterly Progress Report No. 6³ was issued.

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3. Cementing of Geothermal Wells, Progress Report No. 6, July-September 1977, BNL 50738.

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APPENDIX 1

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

TECHNICAL REPORT NO. 2
October to December, 1977

from

DEPARTMENT OF MATERIALS AND CHEMICAL ENGINEERING
UNIVERSITY OF RHODE ISLAND
KINGSTON, RHODE ISLAND

to

PROCESS TECHNOLOGY DIVISION
DEPARTMENT OF APPLIED SCIENCE
BROOKHAVEN NATIONAL LABORATORY
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I. Introduction

This report covers the highlights of work completed under the contract during the second quarter, September to December, 1977. The major efforts were made in the following areas: phase stability in the system Al_2O_3 - P_2O_5 - H_2O under geothermal conditions, preparation of CaO - Al_2O_3 - SiO_2 glasses for determination of leach rates in phosphate solutions, stability of phosphate cements at geothermal conditions, viscosity of phosphate cement slurries, and corrosion of steel by phosphate solutions at geothermal conditions.

A summary of our findings which have particular significance to geothermal well cementing is listed below:

- Small phosphate cement cylinders have passed initial stability tests in 25% brine and water at 200°C.

- In the system Al_2O_3 - P_2O_5 - H_2O , although berlinite, the quartz form of AlPO_4 , is the major phase observed at geothermal conditions, there is some evidence for the existence of an alumino-phosphate hydrate which co-exists with an aluminum hydrate which could act as a cementing phase and remain stable at geothermal conditions.

- Initial corrosion tests on stainless steel show phosphate liquids severely corrosive at 200°C. Tenth gram samples of 316 stainless are totally digested in 1 ml of 40% H_3PO_4 in 28 hours.

II. The System Al_2O_3 - P_2O_5 - H_2O

In all known glass-bonded phosphate cements the alumina-phosphate reaction is important in the cementing of the materials.

We are studying this system at 200°C to obtain data on the reactions of alumina with phosphate solutions which may occur in a geothermal setting.

The three binary systems have been studied. The system $H_2O - P_2O_5$, the phosphoric acid system has two binary compounds H_3PO_4 (m.p. 42.35°C) and the hemidrate, $H_3PO_4 \cdot 1/2 H_2O$ (m.p. 29.3°C). (1). A volumous literature exists on the system $H_2O - Al_2O_3$ with reference to the hydrates of alumina. (2). Under geothermal conditions, boehmite and diaspore, both polymorphs of $Al(OH)_3$, are stable up to 370°C and 385°C, respectively but gibbsite, $Al(OH)_3$ was not observed under equilibrium conditions. (3). There are two reported phases in the system $Al_2O_3 - P_2O_5$. (4). The metaphosphate, $Al(PO_3)_3$ and the orthophosphate, $Al PO_4$, are the only stable anhydrous aluminum phosphates.

$Al PO_4$ is isomorphous with SiO_2 and for that reason it has been widely studied (5,6). The compound can crystallize with a quartz structure, (the mineral, berlinite) a tridymite structure and cristobalite structure. It shows some solid solution in silica and displays many of the metastable reactions shown by silica.

This ternary system has been investigated by Brosheer et al at 25°C, 50°C and 75°C. (7). Martin and Guerin have studied the system at 60°C (8) and Sveshnikova has presented data at 90°C (9). These authors report a total of seven alumino-phosphate hydrate phases. The ratio of moles of Al_2O_3 to P_2O_5 to H_2O for these compounds is as follows: the hydrates of orthophosphate, 1.1.2, 1.1.4, and 1.1.6; the hydrates of pyrophosphate, 1.2.5 and 1.2.9; a single

hydrate of metaphosphate 1.3.6 and a single hydrate of a sesquicompound 2.3.8. The agreement between authors is not perfect but much of the data are mutually consistent. A composite phase diagram for the system $\text{Al PO}_4 - \text{H}_2\text{O}$ is given in figure 1. The data is derived from the above references plus data generated by this study and reported below. Solubility data at elevated temperatures are given in the work of Stanley (10). Retrograde solubility was observed by both Gruner and Stanley and Stanley states that hydrates begin to form below 140°C . The retrograde solubility of aluminum phosphate in solutions is severe for 6 molar phosphoric. Three moles of Al PO_4 can be dissolved per liter of 6 molar phosphoric at 145°C but only 0.2 moles can be dissolved at 245°C .

Our work on this system during this reporting quarter concentrated on the 200°C isothermal section. The runs made are tabulated in table 1. Shown there are the phases observed after each firing. In every case 0.05 micron Al_2O_3 with a trace of $\text{P}_2\text{O}_5 - \text{H}_2\text{O}$ solutions were made from concentrated H_3PO_4 . The solutions were mixed with the Al_2O_3 and sealed in glass ampules and heated to 200°C . The inside pressure is approximately 245 psia and most of the sealed tubes held up without explosion.

Figure 2 shows the compositions of the runs made and the phases observed in each glass ampule. Figure 3 shows the 200°C isotherm and the two-phase tie lines joining alumino phosphate solutions with crystalline Al PO_4 , berlinite. Figure 4a shows single crystals from one run and the morphology was extremely uniform in all runs.

There is still some uncertainty about the area between

Figure 1. Approximate stability relations of hydrates of AlPO_4 at low pressure (less than 200 psi).

Table 1 - Phases observed in
 Al_2O_3 - P_2O_5 - H_2O firings at 200°C.

No.	Initial composition %			Reaction Time (hr)	Final Phases
	Al_2O_3	P_2O_5	H_2O		
1	5	38	57	220	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
2	10	36	54	220	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
3	5	47.5	47.5	220	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
4	10	45	45	220	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
5	1	49.5	49.5	1.5	$\text{Liq.} + \text{Vap.}$
6	2	58.8	39.2	1.5	$\text{Liq.} + \text{Vap.}$
7	3	58.2	38.8	4	$\text{Liq.} + \text{Vap.}$
8	4	57.6	38.4	9	$\text{Liq.} + \text{Vap.}$
9	5	57.0	38.0	48	$\text{Liq.} + \text{Vap.}$
10	6	56.4	37.6	121	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
11	4	59.14	36.86	46	$\text{Liq.} + \text{Vap.}$
12	5	58.52	36.48	19	$\text{Liq.} + \text{Vap.}$
13	6	57.90	36.10	75	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
14	7	57.29	35.71	75	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
15	8	56.67	35.33	71	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
16	2	49	49	17	$\text{Liq.} + \text{Vap.}$
17	3	48.5	48.5	22	$\text{Liq.} + \text{Vap.}$
18	4	48	48	41	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
19	1	39.6	59.4	1	$\text{Liq.} + \text{Vap.}$
20	2	39.2	58.8	50	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
21	3	38.8	58.2	50	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
22	1	19.8	79.2	82	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
23	2	19.6	78.4	93	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
24	1	29.7	69.3	93	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
25	2	29.4	68.6	93	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
26	1	4.95	94.05	312	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
27	2	4.9	93.1	312	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
28	1	9.9	89.1	312	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
29	2	9.8	88.2	312	$\text{AlPO}_4 + \text{Liq.} + \text{Vap.}$
30	2	0	98	116	$\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} + \text{Liq.} + \text{Vap.}$
31	5	0	95	116	$\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} + \text{Liq.} + \text{Vap.}$
32	10	0	90	116	$\alpha\text{-Al}_2\text{O}_3 + \gamma\text{-AlOOH} + \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} + \text{Liq.} + \text{Vap.}$
33	5	4.75	90.25	113	$\text{AlPO}_4 + \text{AlPO}_4(\text{T}) + \alpha\text{-Al}_2\text{O}_3 + \text{Liq.} + \text{Vap.}$
34	10	4.5	85.5	113	$\text{AlPO}_4(\text{T}) + \text{AlPO}_4 \cdot \text{H}_2\text{O} + \alpha\text{-Al}_2\text{O}_3 + \text{Liq.} + \text{Vap.}$

H_2O - Al PO_4 and the hydrated alumina phase. Reaction times for equilibria in the almost pure water solution seems to be longer than with acidic liquids. Some evidence has been observed for a hydrous Al PO_4 in this area. Also, the tridymite polymorph of Al PO_4 has been observed in this area of the diagram. Whether this is a stable phase or a transitive phase is not known at this time. More work is being done in this area. Also, the high P_2O_5 area of the diagram is not worked out and some runs using the orthophosphate and the metaphosphate are underway.

Figure 4b shows a spherulitic growth of aluminum hydrate which is not identified but occurred in both of the runs made up of pure Al_2O_3 and water. The growing phase forms hard nodules at 200°C and could be as cementing phase at geothermal temperatures. The X-ray pattern does not match that of any reported gibbsite, boehmite or diaspor phase. Microscopic examination of the nodules show radiating needle-like crystals which terminate on the surface of the growing sphere with cubic faces. In several cases, these spheres are welded together into a solid mass. Work is continuing to determine if this phase is stable and also to determine the chemical nature of the phase.

III. Glass leach rates

One of the necessary features of a geothermal well completion cement is controllable setting time. It is one of the goals of this project to design a series of glasses which will react with a phosphate liquid at various temperatures and set up at different rates. Since the cementing reaction is caused by leaching of

Figure 2. The system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ showing compositions of runs made and resulting phases.

- - Liq. + Vapor
- ▲ - AlPO_4 + Liq. + Vapor
- - $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ + Liq. with x unknown + Vapor.
- ▼ - $\alpha\text{-Al}_2\text{O}_3$ + $\gamma\text{-AlOOH}$ + $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ + Liq. + Vapor
- - AlPO_4 + AlPO_4 (Tridymite form) + $\alpha\text{-Al}_2\text{O}_3$ + Liq. + Vapor
- - AlPO_4 (Tridymite form) + $\text{AlPO}_4 \cdot \text{H}_2\text{O}$ + $\alpha\text{-Al}_2\text{O}_3$ + Liq. + Vapor

Figure 3. Phase relations at 200°C in the system
Al₂O₃-P₂O₅-H₂O.

Figure 4a. Rhombohedral single crystal of Al PO_4 - berlinite grown at 200°C . Run No. 15. (Mag. 50X).

Figure 4b. Spherical mass of radiating crystal of an unidentified alumina hydrate. Grown in the 5% Al_2O_3 :95% H_2O run at 200°C for 116 hours. Run No. 31. (Mag. 300X).

various ions from the glasses, a knowledge of the leach rate of ions from silicate glasses by the action of phosphate liquids is necessary.

The leach rate of Ca^{++} and Al^{+++} from silicate glasses will be studied as a function of silica content in the glasses and temperature. Glasses containing equal amounts of CaO and Al_2O_3 and varying in silica from 80% to 50% are being prepared. The powders (CaCO_3 for CaO) are mixed thoroughly and melted in a platinum crucible. Fibers are drawn, cooled, crushed and examined under the microscope for homogeneity. Once the glass is "fired" a series of fibers are drawn and cut into one inch lengths. These fibers of known weight, volume and surface area will be immersed in 30 per cent P_2O_5 solution and their weight loss will be measured as a function of time at 40°C , 90°C and 140°C .

The melting and fiber drawing tasks have been completed for two of the glasses. The leach rate studies have been started for one of the glasses at 40° .

IV. Slurry viscosity, cement stability and steel corrosion.

Some experiments were conducted using a Brookfield viscometer to determine the viscosity of slurries of alumina powders and phosphate liquids. With 1 powder, the powder is not totally wetted at 50 weight per cent water and therefore the slurry is not pumpable. Some thixotropy was noted. At low spindle speed, somewhat higher viscosities were measured. The average viscosities are given in table 2.

Table 2

Viscosities of Alumina Slurries

Weight per cent		
water	l Al_2O_3	viscosity (centipoise)
55	45	2367
60	40	1710
65	35	620
70	30	70

70 volume per cent slurries

% of H_3PO_4	viscosity (centipoise)
0%	70
10%	45
20%	153
40%	253

To determine the effects of the more viscous phosphate solution on the slurry viscosity a series was run keeping volume constant. As shown in table 2 the viscosity passes through a minimum and then increases. This means that dilute phosphate solutions can be loaded more heavily than water and still remain pumpable, but more concentrated phosphate solutions can not be pumped at the powder/liquid ratio of water/cement slurries.

With the very thick slurries, accurate determinations with the Brookfield viscometer were difficult. The simple Zahn cup viscometer which is used for viscosity measurements of ceramic and paint slurries may give reproducible results and be ideally suited for relating pumpability to powder-liquid ratio. This device is on order and will be tested in the next quarter.

Some qualitative tests were made on phosphate cements stability in water and 25% brine solution at 100°C and 200°C. While no strength tests were made, the samples maintained their integrity and had considerable strength after the tests.

Three phosphate cement samples were boiled in water for 10 days and showed a 6 per cent weight loss. Three samples were boiled in brine for seven days. They showed about a three per cent weight loss. Small cylinders of cement (1/2 inch high x 1/4 inch diameter) were sealed in water and brine at 200°C. They have been at temperature for ten days. They did not disintegrate and show no loss in integrity. No weight loss information is available as yet.

As part of the effort to select materials for the construction of high temperature autoclaves to contain phosphate solutions a corrosion study was performed on 316 stainless steel. Tenth gram samples (4 x 4 x 1 mm) were sealed in glass tubes with 40, 50 and 60 per cent phosphoric acids. The amount of acid was 1 ml. in each case. These tubes were heated to 200°C. At the end of 28 hours, all steel pieces were totally digested in the acid leaving a deep green solution.

These observations preclude the use of high phosphoric acid solutions in the geothermal environment if setting were very slow. However as seen in figure 2 as a phosphate solution reacts with an alumina containing cement powder, the solution becomes less acidic. As Al PO_4 is formed at 200°C the phosphoric acid will change into almost pure water. Further studies will be made in this area.

V. Future Plans

- The 200°C isothermal section of the system $\text{Al}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$ will be completed.
- Studies will begin on the 200°C section of the system $\text{CaO} - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$.
- Work will continue on phosphate cement stability at elevated temperatures in water and brine.
- The leach rate of Ca^{++} and Al^{+++} from silicate glasses in phosphate liquids will be determined.

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APPENDIX 2

C00/4190-1

DEVELOPMENT OF GEOTHERMAL WELL COMPLETION SYSTEMS

Phase I Report

for period July 1, 1977 - September 30, 1977

CONTRACT NO. EG-77-C-02-4190

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ABSTRACT

Information has been gathered from companies experienced in geothermal well cementing. Most companies expect problems to develop as well conditions become more severe, and the wells age. Such things as thermal shock effects, high temperatures, and high reservoir permeabilities point out a need for light weight cements with good bonding and compressive strength characteristics. Previous high temperature cement research has led to doubts concerning the stability of pozzolan cement systems. Also, the use of silica flour at up to 40 percent concentration has been shown to be beneficial. Initial test procedures for cement systems in this present study will enable many cement formulations to be screened before long term evaluation under conditions of high temperature, high pressure, and brine contact is started.

Introduction

This report describes research carried out during the first phase of ERDA Contract EG-77-C-02-4190, for the development of geothermal well completion systems.

During the period of May 1 to September 30, 1977, background data on high temperature cementing and related problems was gathered. Many existing publications on high temperature cementing were studied, and Dowell's proprietary information on research and records of wells cemented were reviewed for information applicable to this project. (1-4) A major source of information for this study was a series of interviews with engineers and drilling personnel of companies having geothermal drilling and completion experience. This enabled us to define current cementing practices and problems and help set objectives for future research. Initial test procedures were then designed based on this background study.

The following is a list of variables to be determined in the Phase I study. The first seven are from our original proposal and the last four were suggested as we began our study.

1. Expected well life in different type fields.
2. Expected characteristics of geothermal fluids.
(Brine or steam)
3. Static and circulating temperatures expected for the various types of fields.
4. The weight range needed for cementing slurries.

5. The thermal variations expected in the life of a well.
6. The type of drilling muds expected to be used in geothermal wells.
7. Economic limitations on geothermal completion systems.
8. Minimum strength desired for cement and acceptable strength.
9. Porosity and permeability, desired and accepted.
10. Heat transfer properties of cement.
11. Bonding strength desired or acceptable, to pipe, to rock.

SUMMARY OF INFORMATION GATHERED IN OPERATOR INTERVIEWS

1. Wells are rarely cemented under geothermal conditions. Drilling programs of all the operators responding to our questions call for setting surface and production pipe above the reservoir. Bottom hole temperatures, where measured, seldom exceed 116°C. Mud flow line temperatures are 93-104°C.

In some cases, slotted liner is hung through the producing zone, but cementing the liner is not considered critical.

In one area the producing zone is so shallow that the reservoir may be encountered before surface pipe has been run. In this case the hole is cooled by circulation to a temperature where the cementing operation can be conducted without problems. This is thought to be in the 116°C range although the operator did not have a precise measurement.

2. Rock formations are highly permeable. The nature of an economical geothermal reservoir is such that large quantities of hot water or steam must be produced from each well. Permeabilities therefore must be in the darcys. Highly fractured rocks and poorly consolidated sandstones are the most common reservoir rocks.

3. Chemistry of reservoir fluids varies from fresh water to extreme salinity. Dry steam fields containing relatively few salts have low percentages of noncondensable gases, the most noticeable being H_2S . Hot water fields in some cases have virtually no salt and only a small percentage of silica, but in one major field salinities as high as ten times sea water are reported.
4. Pressures are seldom above hydrostatic except geopressure zones. Dry steam fields report measured reservoir pressures that vary from 3500 to 3800 kPa at depths from 900 to 3000 m. In hot water fields, pressures at the bottom of a 3000 m hole will be less than 3500 kPa. Reservoirs appear to be slightly under pressure relative to hydrostatic in some fields.

Exceptionally high pressures of 69,000 to 138,000 kPa have been reported for geopressed zones which are found from 3700 to over 6000 m deep.

5. Bottom hole static temperature and bottom hole circulating temperature data are often unreliable and misleading. Published reservoir temperatures vary as much as 66°C higher than data reported by the operator for the field. This is because many authors do not have proprietary data retained by the operator and often make unwarranted

assumptions. Also, the promotional nature of many geothermal ventures leads to a slight exhuberance on the part of the authors. The operators themselves use different methods to measure temperatures with results that vary as much as 10°C for the same well.

The highest accurately measured temperature reported to us is 357°C. One well was reported to be higher, but all others were less than 316°C.

6. Thermal shock effects on cement may be significant. All operators expressed concern over the cement to pipe bond, when subject to the temperature cycling of drilling, testing, shutting in, and producing. In areas where feasible, wells are left on a bleed system to keep temperature up, but in most areas this is not possible.

Several operators expressed concern over the possible changes in permeability from microfractures in the cement sheath induced by thermal shock.

GENERAL DIRECTION OF PHASE II RESEARCH

Long Term Strength

Although all operators do not currently cement wells under conditions of high temperatures, the cement will ultimately be subjected to the maximum reservoir temperature under production. Since these wells are expected to produce for twenty to thirty years the cement will be subjected to these temperatures for most of the life of the field.

For these reasons, long term strength has been given priority in our research effort.

Bond Strength

Information on bond strength is inconclusive but the likelihood of bond failure as a result of thermal shock or long periods of time at high temperatures suggests the need for careful research along this line.

Lightweight Cements

The nature of the geothermal reservoir, high permeability, makes it imperative that cement formulations developed have low density or other characteristics that will prevent loss of cement or formation damage.

These three criteria, long term strength, bond strength, and lightweight, are often incompatible with each other. As a result, many cement formulations will have to be screened and evaluated.

In addition, it is expected that as geothermal exploration develops, higher temperatures may be encountered in rocks of very low permeability. This will require cementing pipe in the hottest zones to enable stimulation techniques to be employed. While wells are not now cemented under conditions of high temperature, it is very likely that they will be in the future.

We have selected the following test criteria for our long term tests. It is expected that hot water tests will occupy 75% of the effort, with dry steam tests 20% and dry air tests 5%.

TEST ENVIRONMENTS

I.	Dry	225°C 325°C
II.	Dry Steam Dry Steam + H ₂ S	225°C 325°C
III.	1. Hot Water	Brackish < 10,000 ppm TDS 225°C 325°C
	2. Hot Water	High salinity - 200,000 ppm TDS 225°C 325°C
Pressures - 3500 kPa - dry steam 35,000 kPa - hot water 69,000 to 138,000 kPa - geopressure		

The general guidelines we will follow during the screening tests will be as follows:

INITIAL TEST CRITERIA

Placement Ability - 3-4 hours retardation at BHCT

Compressive Strength - Greater than 3500 kPa
at 24 hours for
lightweight cements

Permeability - Less than 0.1 md to water

Stability - Strength loss no greater than 30 percent
in 30 days

BACKGROUND INFORMATION PROVIDED BY COMPANIES INTERVIEWED

On the following pages the information gathered from companies operating geothermal wells, in a series of contacts by mail, phone, and in interviews with drilling personnel is listed. All responded to some extent. Most of the companies were very cooperative although some provided significantly more information than others. Some of the companies utilized consultants for drilling and completion guidance and therefore had little information on cement problems. Usually they referred us to the service companies who did the cementing to provide specific strength, permeability, weighting, and cement formulations. Specific data is reported where provided but some of our questions were thought to involve proprietary data and were not answered, particularly data on reservoir temperatures and costs.

It was originally planned to characterize each geothermal field by the geochemistry of the waters and then report information on each company's experiences in that field without identifying the company by name. Unfortunately, because there are so few geothermal fields and so few companies operating in each, it was felt that the geochemical data were too distinctive and would serve to readily identify each operator providing information.

In order to persuade the companies contacted to cooperate freely, we agreed to report all information given by each separately as "Company A", "Company B", etc., and make few, if any, distinctions between fields.

The small size of the geothermal industry makes even this approach difficult to use in protecting anonymity but most of the companies preferred it.

"Company A"

The average age of wells has been four years, with the oldest in service eight years. No workover operations have been required on ninety percent of the wells. A few have required squeeze cementing and casing replacement. Each well has a planned life of 30 years but it may be possible to continue in production longer. Wells may decline in production from formation plugging. This operator believes that these wells can be revitalized but no attempts have been made so far. No wells have been lost from cement failures.

Cement formulation used:

Class G, 1:1 perlite

40% silica flour

3% gel

Retarders, friction reducers

1.52 kg/l slurries were used on surface pipe, and 1.87 to 1.92 kg/l neat G plus 40% silica flour was used on production string. It is preferred to use as light a slurry as possible because of low fracture gradient. No correlations have been noted between cement density and stability. Two to three hours of pumping time, including safety factor, is normal.

Geothermal Fluid Composition

Dry Steam contains up to two percent noncondensable gases. One to fifteen percent of the noncondensibles is H_2S which does not appear to affect cement. Few abrasive solids are contained in steam after initial flow begins. Fifteen percent of the fluids are reinjected. These fluids could be used to mix cement but it is probably unnecessary as other sources are available.

Temperature

Reservoir temperature is 246-249°C in dry steam fields as measured by wireline logging tools. The mud flow line temperature is usually 104°C when drilling near the reservoir. Downhole circulating temperatures are 150°C maximum and can be lowered by circulating before cementing.

Depths vary from 1500 to 3000 m and maximum pressures are 3500 kPa for dry steam and hydrostatic for other parts of the field.

Thermal Variations

Temperatures the cement sheath is subjected to will vary 93°C during drilling and completion. Conditions for production string cements will change from 116 to 204°C during WOC time.

During testing and production a change of 150 to 232°C in less than one hour may occur. This may fracture cement. Maximum temperature encountered was 254°C in dry steam fields, and 288-316°C in hot water.

Drilling Muds

Standard bentonite gel - water mixtures are used. Caustic and other additives are minimized because of environmental aspects of drilling permits.

Rocks drilled are serpentine, graywacke and sandstones. Serpentine will make mud but otherwise it does not present a problem.

This Company would be willing to change muds if necessary to improve cement jobs.

Casing Programs

Usual casing practice is to cement 150 m of 20 in. conductor to surface, followed by up to 760 m of 13-3/8 in. surface pipe also cemented to surface. Great care is taken to insure complete

return of cement in the annulus to the surface. If the cement falls back, it is topped to the surface. This prevents casing elongation or at least minimizes it. The 9-5/8 in. production string is set above the reservoir by either hanging at approximately 700 m or in some cases cementing to surface. The wells are always completed open hole.

Approximately 100 barrels of water are used as a spacer and occasionally hydrazine is used as a flush.

The cement cost is up to \$40,000 per well - a 10% increase in cost could be accepted if performance improvements were demonstrated. WOC time is seldom a factor as up to 24 hours is required to connect blowout preventers.

Minimum Strengths

Class G, 1:1 perlite plus 40% silica flour - 7580 kPa 24 hours
Neat G and silica flour - 15,860 to 16,550 kPa after 8 hours
This company would like higher strengths.

Porosity and Permeability

No specific data is available on permeability of cements now in use. It is expected that permeability would increase with time but the amount is unknown.

Heat Transfer Properties

The company does not consider it important.

Bonding

It is believed that the bond of cement to pipe is quite good. Failed casing recovered during a workover had a cement sheath which was strongly bonded to the casing. This well had experienced the normal stresses of drilling and testing. Bond strength was not quantified.

This company believes that thermal shock probably will cause failure of the cement-pipe bond in some cases.

Casing does not elongate if properly cemented. Special care is taken to complete cement sheath from surface to T.D. of 13-3/8 in.

All wells are placed on bleed system after initial tests to prevent thermal shock.

No bond logs are available for examination.

"Company B"

No wells are currently on production. Several have been drilled and tested during the last six years. Workover has consisted of replacing slotted liners on some wells. Liners are hung and not cemented.

Cements used:

Class G, 1:1 perlite

35% silica flour

2-3% gel

With up to 0.5% friction reducers.

Water is used as a spacer. Slurries are retarded to provide 2-3 hours emplacement time including safety factor.

Wells are designed to last thirty years and the only problems expected will be occasional sand inflow which will require removal.

Fluid Characteristics

Reservoirs are in low salinity brines (2500 to 3800 ppm TDS) and in saline (44,000 ppm) waters. In the lower salinity reservoirs few salts or gases are troublesome. In the high salinity reservoirs carbonate and sulfate minerals as well as halite may cause formation plugging. It is not necessary to use reservoir fluids as mix water as other sources are available. Spent fluids will be reinjected.

Temperatures

Precise reservoir temperatures are classified, but low salinity fields vary from 177 to 204°C. Higher salinity fields are over 204°C. These temperatures are measured by wireline logging

instruments. BHCT is not measured, but probably does not exceed 104°C. All wells can be cooled by circulating. Mud flow line temperatures are less than 93°C. Depths vary from 1200 to 2100 m and pressures are hydrostatic.

Weight Range

Slurries are adjusted to 1.44 to 1.56 kg/l range. This company would like to use 1.2 kg/l or less if possible. Low formation pressures are the primary reason for using lightweight cements. No correlations have been noted between cement weight versus stability.

Thermal Variations

During drilling and completion operations temperature cycles of less than 93°C are expected. When undergoing tests, a well can cycle 93°C to over 204°C in less than one hour. When shut in, cooling will be at a lower rate. This company believes that thermal shock may fracture cement but it does not appear to be a problem at this time.

Drilling Muds

Standard bentonite gel muds are used with few additives both to simplify procedures and to abide by environmental restrictions. Mud costs can be up to \$50,000 per well particularly if salt based muds are used. Mud is usually mixed to provide 10 ml or less water loss.

Rock types being drilled include poorly consolidated sandstone and clay.

Economic Limitations

Casing programs include 30 to 60 m of 20 in. conductor cemented to surface, 13-3/8 in. surface pipe is run to a point above the reservoir, depth up to 760 m. Special care is taken to get cement returns to surface when cementing 13-3/8 in. casing. No spacers or scratchers are used but centralizers every 120 m are used. 9-5/8 in. or 8-1/2 in. liner with 1/4 in. slots is hung in the 13-3/8 in. pipe and extends through the reservoir. It is not cemented. Average cement cost is \$17,000 to \$20,000. WOC time is not a factor.

Strength

Compressive strength data is not available. Referred to service company literature.

Porosity and Permeability

Data not available.

Heat Transfer

Heat transfer properties of cement are not considered important.

Bonding

This company believes that bond to pipe is good and will hold with time. Variations in temperature will not cause bond failure. Cementing of surface pipe is considered to be the key to successful completion of geothermal wells. If 13-3/8 in. pipe is cemented to surface then pipe will not elongate and cement to pipe bond will remain intact.

"Company C"

Well Life

No wells are currently producing but design life is expected to be 20-25 years. Wells are cemented using the following slurry formulations:

- Class B, 1:1 perlite
- 40% silica flour
- 2% gel
- 0.5% friction reducer
- 1 to 3% retarder

Weight Range

Weight range of slurries now in use is 1.57 to 1.63 kg/l.

This company would like to have lighter cements because of the low fracture gradient.

Water is used ahead of the cement to clean the hole.

Geothermal Fluids

Salinity of this hot water field is very low, 1500 ppm TDS. Water does not contain any abrasive solids and can be used as cement mix water. Spent fluids will be reinjected.

Temperature Data

Static reservoir temperatures are greater than 204°C as measured by wireline logging tool. Mud flow line temperatures are as high as 93°C. Wells may flow while drilling. Depths are 305 to 915 m and pressures are hydrostatic.

Thermal Variations

During drilling, temperature changes of 93°C are possible in a few hours. Under testing, wellbore temperatures can change 93°C to 204°C in less than one hour. The operator does not know if this fractures cement.

Drilling Muds

Standard fresh water bentonite gel is used with some lost circulation materials. Mud viscosity of 32-36 cp is usually maintained. Rock types are principally granite.

This operator would change muds if the cement system required it. They emphasized a need to clean the well with some spacer or wash before cementing.

Economic Limitations

The casing program now in use includes 30 m of 20 in. conductor pipe, and 305 to 610 m of 13-3/8 in. surface pipe. Some wells are completed with only 13-3/8 in. casing. A few have 9-5/8 in. pipe either hung and cemented or cemented to surface.

Typical well completion costs range from \$350,000 to \$450,000. Cement costs are \$35,000. This company would pay 10% more for improved cement. WOC time is not a factor.

Strengths

Compressive strength of cements now in use is 15,860 kPa at 24 hours, with not less than 6895 kPa after extended time.

Porosity and permeability data are not available.

Heat transfer properties are not considered important by this operator.

Bond

This company believes that the cement does not bond well to the pipe but acts as a "snug" fit which both supports the pipe and provides an effective seal. Variations in temperature therefore have no effect on bond strength. The casing elongates 0.10 to 0.35 m during testing. Bond logs have been run and may be made available.

"Company D"

Well Life

The longest period a well has been in use is seventeen years. In one area fifty percent of the wells require no additional work after completion. The rest require squeeze cementing and some casing replacement. The average well age is 12 years so far with a planned life of 25-30 years.

The cement formulation used on early wells is unknown; however, an analysis of this cement has indicated that perlite was probably used to extend the slurry. The lack of free quartz in the X-ray and the presence of calcium hydroxide, some of which has apparently converted to calcium carbonate, indicate the cement was not stabilized and has deteriorated.

Cement formulations using pozzolan as an extender have been tried in this area, but not enough time has elapsed for evaluation of effectiveness. Laboratory studies indicate probable strength retrogression with time.

Recently drilled wells in this area use a cement based on the following:

- Class G, 1:1 perlite
- 40% silica flour
- 2% gel
- 0.5% friction reducer
- 0-1% retarder
- Water ratio: .46:1
- Density: 1.46 kg/l

Standard methods of emplacement are used with water as a spacer. Cement is retarded for 1 hour pumping time with 1/2 hour safety factor.

Characteristics of Geothermal Fluids

Dry Steam contains 1-2% noncondensable gases which will decline to 0.5% with production. Analysis of the noncondensable gases by weight percentage:

CO ₂	82.5	
CH ₄	6.6	
H ₂	1.4	
N ₂ + A _r	1.2	
H ₂ S	4.5	(can be as high as 15)
NH ₃	3.8	

Hot water and brine fields have varying percentages of dissolved solids that range from fresh through brackish to extreme salinity.

Temperature

Reservoir temperatures vary from 177 to over 371°C. The static temperatures are calculated from temperatures recorded while taking deviation surveys. In a few cases static temperatures were measured by wireline logging methods. Dry steam reservoir temperatures are 240°C. Most hot water fields are less than 260°C. One brine field is much greater than 260°C. The highest temperature is 399°C. This was determined on one

measurement in which the logging tool (rated to 399°C max) broke during the run. It is not known whether the device broke from the heat or from other causes.

Circulating temperatures vary between 93°C and 204°C depending on whether the measurements are taken in the reservoir or above it. Mud flow line temperatures are usually 82°C. Temperatures downhole can be lowered by circulating before cementing.

Slurry Weight Range

Cement slurries currently used vary from 1.52-1.68 kg/l. Because of the low formation pressures, and low fracture gradients in most reservoirs, weights as low as 1.12 kg/l would be ideal. No correlation has been noticed between cement weight versus stability.

Thermal Variation

During drilling and completion of a well the range of temperature variations is probably less than 93°C. However, when a well is tested the casing and cement are subject to 149 to 204°C temperature changes during the testing period of a few hours (1 to 6). After placing the well on production no significant variations occur unless workover of the well is necessary.

Dry steam wells are left on a bleed system after testing which reduces thermal shock. Hot water wells do not presently employ

a bleed system, but probably will in the future. This operator believes that thermal shock will definitely fracture cement systems now in use. This is not thought to be a serious problem at present.

Drilling Muds

Wells are drilled with both air and mud. Mud systems are usually standard gel-water mixtures. Additives such as lignin-tannins and acrylates, sepiolite, and caustic are sometimes used. Mud systems are rarely changed except in cases of low formation stability.

Drilling muds would be changed to accommodate newly developed spacers and cements if overall costs and performance warrant.

Rock types drilled vary depending on field. Tuffs, andesite, basalt, serpentine, sandstones, shales and graywacke are most commonly drilled.

Economic Limitations

Casing programs now in use vary with fields but usually include 30 to 150 m of 20 in. conductor cemented to surface, 305 to 760 m of 13-3/8 in. surface pipe cemented to surface, 9-5/8 in. production pipe hung or cemented to surface.

Use of specialized equipment such as scratchers and centralizers varies with each field. Completion costs vary widely, but cement costs are as high as \$50,000 per well.

Strength

The minimum strength desired for cement is 6890 kPa, but 689 kPa after 25 years of service is acceptable. Cements now in use are 20,685 kPa. Inadequate data are available to project downhole strengths of cements now in use.

Porosity and Permeability

Little information is available, but some data from wells which failed after five to seven years of service indicate a limit of no more than one md permeability to gas after 25 years.

Heat transfer properties of cement are not considered important by this operator.

Bonding Strength

Information on bonding to pipe or rock is inconclusive at this time. This operator believes that variations in temperature cause failure of cement to pipe bond. Casing elongates as much as 0.76 m, while the cement sheath does not elongate at all. Self-stress cements may be desirable.

Cement bond logs have been run but appear to be inconclusive.

DOWELL'S HIGH TEMPERATURE CEMENT RESEARCH

Dowell has been conducting research on cement systems for geothermal wells since the early 1960's; as a result, a great deal of useful information has been acquired.⁽¹⁻³⁾ This summary of Dowell's high temperature cement research program reports the principal findings concerning the physical and chemical behavior of cement systems exposed to conditions thought to exist in a geothermal environment.

Testing has been performed on an extremely wide range of systems. Over a thousand tests have been run on approximately 160 different systems incorporating nearly every type of cement, cement additive and cement extender commonly used by the well cementing industry. These cement systems have been exposed to saturated steam pressures at temperatures ranging from 110°C to as high as 1093°C, and cured for periods ranging from one to 720 days.

Dimensional and Weight Stability

The only systems that change more than one percent in size and five percent in weight during exposure are high-water extended cements. They tend to increase in size and weight as they deteriorate.

Stabilized pozzolanic cements, especially those containing fly ashes, occasionally develop a roughened surface or nodule along a water line.

Strength

Neat Portland cement systems weaken greatly during the first day of heating at both 204 and 316°C; however, those systems containing the API recommended amount of water maintain compressive strengths above 3500 kPa. 3500 kPa is thought to be the minimum strength required for proper operation of a well.⁴ Extended systems with 100 percent water by weight of cement and no silica drop below 1380 kPa during the first month and complete disintegration can occur.

The addition of 30 to 40 percent silica by weight of Portland is sufficient to stabilize most systems against high temperature strength retrogression. Any additional silica acts simply as an extender or filler. Reduction of the amount of mix water reduces the degree of strength retrogression but not as effectively as the addition of silica. Class J cement, essentially a mixture of dicalcium silicate and quartz, requires no additional silica for stability.

The stabilized cement formulations can tolerate most additives without strength retrogression. This includes those additives that do not change or react with normal cement hydration such as weighting agents, extenders and lost circulation materials. It is important to realize that extended systems are not necessarily as strong as normal water systems. Test results show that extended systems with silica do not experience significant strength retrogression upon heating.

A notable exception is that pozzolans are detrimental. Fly ashes can cause more strength retrogression than natural pozzolan materials. Fly ash systems tend to gain strength for the first 30 days at 316°C and 180 days at 232°C then begin to lose strength. This type of degradation occurs according to a different mechanism than the usual high temperature deterioration.

Permeability

The permeabilities of all cement systems aged at 232°C and 316°C are high as compared to most cements maintained below 93°C. Most systems cured at 93-107°C have permeabilities in the range of one microdarcy and do not increase greatly in permeability when maintained at this temperature under moist conditions. The permeability increase is usually more rapid at 316 than at 232°C. Some neat G and A cement systems at 316°C increase in permeability from 0.001 millidarcy to six or eight millidarcys on heating one day and thereafter do not change appreciably.

Permeability increase is less severe with silica stabilized systems. These systems usually stabilize at 0.07 to 0.2 millidarcys. Reduced permeability can also be achieved in a neat cement with a very low (32 percent) water content. Portland systems with 35 percent silica flour and Class J cement slowly gain permeability over several months. Additives, except fly ash, generally have little effect; however, increased water results in increased permeability. Fly ash cements give a delayed increase in permeability; thus, it can be surmised that permeability varies indirectly with strength.

X-Ray Analysis

The chief composition of all the cement systems is non-crystalline. Tobermorite ($C/S = 0.833$) is the principal crystalline phase below 150°C as detected by X-ray. After one day of heating at 232 and 316°C the tobermorite converted to alpha dicalcium silicate which is a weak porous component of heated cement accounting for most of the initial degradation. Addition of 35 percent silica to Portland cement is sufficient to greatly reduce the amount of alpha dicalcium silicate formed. Instead, a much stronger cement component, xonotlite ($C/S = 1.00$), is formed on heating. These chemical transformations occur within the first month.

The cements containing pozzolan degrade by a different mechanism and require much more time to react. Initially these systems react to form xonotlite as did the other systems; however, over a period of several months at 316°C and a year at 232°C , these compounds convert to a truscottite type ($C/S = 0.66$) compound weaker than xonotlite but stronger than alpha dicalcium silicate hydrate.

Differential Thermal Analysis

Differential thermal analysis (DTA), which measures the internal heat change as a function of temperature, has been used to analyze some systems after aging at 232 and 316°C . By this method it has been established that calcium hydroxide is present in all of the Portland cement systems without silica

even though it is not always detectable by X-ray. The presence of excess alpha quartz has also been confirmed in 50 percent silica systems despite the absence of such information on X-ray diffraction patterns.

Effect of Results on Future Testing

Neat Portland cement systems normally degrade at elevated temperatures by rapid conversion of tobermorite or other hydration products to alpha dicalcium silicate hydrate resulting in low strength and high permeability. This occurs very rapidly; thus, at temperatures of 232°C or above, a test lasting one or two weeks will show the worst conditions that will occur for this type of degradation. These short length tests are adequate to show whether sufficient silica has been added to prevent degradation, and also to show the properties of cements containing non-reactive additives.

There are two exceptions. One is where the Portland cement is stabilized with very fine (-325 mesh) silica. In this instance, the permeability increases slowly for the first 90 to 180 days. The second exception where short term tests are inadequate is when a slowly reactive additive is used such as fly ash. Such systems begin to degrade only after 30 days at 316°C and one year at 232°C.

Principal Conclusions

1. Most Portland cement systems change composition rapidly at 232 or 316°C but stabilize within one or two weeks.
2. The same reactions occur over the 232 to 316°C temperature range but are more rapid at high temperatures.
3. The normal Portland cement strength retrogression caused by conversion to alpha dicalcium silicate hydrate at elevated temperatures is largely alleviated by adding 30 to 40 percent fine silica. The strength is stabilized but the permeability still increases many fold.
4. Most non-reactive cement additives can be admixed in moderation with a stabilized cement system without adversely affecting the temperature stability.
5. A delayed high temperature retrogression occurs in pozzolan extended Portland cement systems, especially those containing fly ash. This is due to a gradual conversion of xonotlite to a truscottite type compound.
6. A high temperature cement should not contain extensive amounts of bentonite, diatomaceous earth, or expanded perlite unless silica is added to stabilize the system.
7. A non-Portland cement, Class J, has the least overall variation of all the systems tested.

INITIAL TEST PROGRAM

The testing program for possible geothermal cement systems must be comprehensive and discriminating. The block diagram of Figure One gives a condensed picture of the proposed Dowell procedure. Cement systems to be tested will include the listed mixtures as well as variations and combinations of the mixtures. A standard system will be tested which represents a typical cement system presently used by the geothermal industry. Each system will first be tested on a high temperature (150°C), high pressure (35,800 kPa) consistometer to determine adaptability to downhole placement criteria. This means the system must be capable of maintaining a liquid state for at least three hours. Systems which can meet this thickening time criterion will be tested in high pressure, high temperature autoclaves for compressive strength. A series of tests up to 28 days is expected to show trends of retrogression or failure to reach minimum acceptable strength. Those systems showing good compressive strength characteristics will be tested for permeability. Poor adaptability of a cement system to geothermal conditions will usually result in permeability increases to excessive levels.

The next test for the surviving cement systems is a bonding test which generally involves cement to steel bond strength.

This test will show poor quality for a cement which either shrinks after set or has little adherence to the steel pipe. Following the bond tests, an ASTM expansion test will be conducted which can help to compliment the bond tests. Again, a shrinkage condition would be undesirable.

The final proposed test in the initial work will be an erosion test to monitor the effects of dynamic steam contact. Any system which shows tendencies of continuous sloughing should be considered unstable and rejected.

Following this testing program the long term tests will be set up to establish stability over many months of geothermal environment contact.

Figure 1.

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- 4 Smith, D. K. Cementing. Dallas: Society of Petroleum Engineers of AIME, 1976.

Appendix A

List of Companies Contacted

AMAX Production Co.	Denver, CO.
Aminoil U.S.A.	Santa Rosa, CA.
Amoco Production Co.	Tulsa, OK.
Anadarko Production Co.	Houston, TX.
Argonaut Enterprises	Denver, CO.
Chevron Oil Co.	San Francisco, CA.
Dow Chemical U.S.A. Oil and Gas Division	Walnut Creek, CA.
Exploration Logging of U.S.A., Inc.	Sacramento, CA.
Geothermal Kinetics, Inc.	Phoenix, AZ.
Geothermex	Berkeley, CA.
Hathaway Engineering	Sacramento, CA.
Intercontinental Energy Corp.	Denver, CO.
Magma Energy	Los Angeles, CA.
McCulloch Oil Corp.	Los Angeles, CA.
Micro Geophysics Corp.	Golden, CO.
Oxy Geothermal	Bakersfield, CA.
Phillips Petroleum Co.	Del Mar, CA.
Republic Geothermal	El Centro, CA.
Southwestern Exploration Assoc.	Tucson, AZ.
Sunoco Energy Development Co.	Dallas, TX.
Thermal Power	San Francisco, CA.
Thermogenics, Inc.	Santa Rosa, CA.
Union Oil Co.	Brea, CA.

Appendix B

List of Abbreviations and Conversion Factors Used in this Report

API	American Petroleum Institute
Ar	Argon gas
ASTM	American Society for Testing and Materials
B	API Class B Portland cement
BHCT	Bottom hole circulating temperature
C.	Celsius (centigrade) temperature
C/S	Calcium oxide to silicon dioxide ratio
CH ₄	Methane gas
CO ₂	Carbon dioxide gas
G	API Class G Portland cement
G,1:1 perlite	One cubic foot (94 lbs) Class G cement combined with one cubic foot (about 8 lbs) perlite
H	API Class H Portland cement
H ₂	Hydrogen gas
H ₂ S	Hydrogen sulfide gas (highly toxic)
in.	Inches
J	API Class J cement
KCl	Potassium chloride salt
kg	Kilogram
kPa	Kilopascal

Appendix B (cont'd.)

l	Liter
lbs	Pounds
m	Meters
max	Maximum
md	millidarcy (unit of permeability)
N ₂	Nitrogen gas
NH ₃	Ammonia
NaCl	Sodium chloride (common salt)
ppm	Parts per million
TD	Total depth of well at time mentioned
TDS	Total dissolved solids
T.T.	Thickening time
WOC	Waiting on cement (to harden) time

Metric to English Conversion Factors

(Degrees C. x 1.8) + 32 = Degrees Fahrenheit

kg/l (or specific gravity) x 8.33 = pounds per gallon

kPa X 0.145 = Pounds per square inch

(kPa ÷ 6.89) = Pounds per square inch

m x 3.28 = Feet

md = One thousandth of a Darcy (see below)

Darcy = A unit of permeability where a fluid of one centipoise (water) under a pressure gradient of one atmosphere per centimeter would flow one cubic centimeter (milli-liter) per second per square centimeter cross section. No normal English equivalent is used.

APPENDIX 3

HIGH TEMPERATURE CEMENTING MATERIALS
FOR COMPLETION OF GEOTHERMAL WELLS

Quarterly Technical Progress Report
September 1977 - November 1977

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HIGH TEMPERATURE CEMENTING MATERIALS FOR COMPLETION OF GEOTHERMAL WELLS

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INTRODUCTION AND SUMMARY

Geothermal energy has come to be recognized as a promising alternate energy source in the United States and many other countries. As a consequence, the Division of Geothermal Energy of the United States Department of Energy has encouraged research in all facets of geothermal energy utilization. To provide assistance in this massive effort the laboratories of Battelle Memorial Institute are applying their research capabilities toward solving many difficult problems confronting the utilities industry trying to commercially utilize geothermal energy. Research programs at Battelle Memorial Institute are concerned with the exploration of geothermal resources, the classification and sizing of geothermal reservoirs, the measurement of geothermal fluid properties, corrosion and scale deposition of geothermal brines, the removal of hydrogen sulfide from geothermal steam, environmental studies, the design and analysis of geothermal power systems and development of cementing materials for completing geothermal wells. The Cements program at Battelle's Columbus Laboratories, sponsored by BNL/DGE-DOE, under the contract number 420825-S, deals specifically with the development of high temperature cementing materials in geothermal applications. Currently, the cementing materials used in the completion of geothermal wells (see Figure 1) deteriorate in the down-hole environment, thus imposing a limitation on the life of the well and on the cost-effectiveness of geothermal energy. In extreme cases, the cement may fail completely and be blown out of the drill hole. The cost of repair or shutting off such a geothermal well is prohibitive.

Research conducted to date has not fully resolved the problem, and further research is urgently needed. Toward this end, the program developed at Battelle Columbus has objectives as follows:

- 1) Evaluation of the performance characteristics for cements currently used in the completion of geothermal wells
- 2) Development of improved cementing materials which can withstand the severe thermal and pressure environment of geothermal wells

GEO THERMAL DRILLING

Figure 1. Schematic representation of the drilling of a geothermal well showing the use of cement to position and hold the steel well castings (Union Oil Company of California).

- 3) Through the use of the knowledge attained from 1) and 2) establishment of a technology base which can provide a guideline or future research efforts if needed.

The immediate objective of the program is to develop one or more cementing compositions suitable for geothermal well completions meeting the minimum requirements set by BNL/DOE. These requirements are as follows:

- Placement ability, involving the capability of three- to four-hour retardation at expected placement temperatures
- Compressive strength of more than 1000 psi 24 hours after placement
- Bond strength to steel casing of more than 10 psi
- Permeability to water of less than 0.1 md.
- Good mechanical stability and low permeability after prolonged exposure at maximum temperature of 750 F to 25% brine solutions, flashing brine or dry steam
- Compatibility of cement with drilling mud
- Non-corrosive to steel well casing.

PROGRAM SCHEDULE

The delay in receiving final approval of the contract from Oak Ridge Operations Office has placed the program slightly behind the planned schedule. However, the experimental procedures have now been fully identified and developed and there are no anticipated experimental difficulties. Therefore, this delay will not present any particular problems to the program.

CURRENT PROGRESS

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

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

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

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

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

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

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

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

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

Based on our understanding of the research problem and guided by the results of the Phase I work, a number of cements, modifiers, and admixtures have been selected for evaluation. A list of the materials selected is given in Table 1. Other candidate materials may be added to this list as the program proceeds. A large number of cementing compositions - literally hundred of batches - will be formulated and screened on the basis of their rheological behavior, and thickening and setting times. If a given cementing composition cannot be formulated (through the use of additives and admixtures) to meet the initial rheological requirements and considerably long thickening times,

TABLE 1. FACTORS THAT CONTRIBUTE TO CEMENTING FAILURES

Type of Failure	Contributing Factor
Premature Setting in Casing	Contaminants in mixing water Incorrect temperature estimate Dehydration of cement in annulus Use of improper cement Plugged cement shoe or collar Insufficient retarder
Failure to Bump Plug	Lodging of plug in head Running of top plug on bottom No allowance for compression Incorrect displacement calculations
Incomplete Mixing	Mechanical failure Insufficient water or pressure Failure of bulk system
Gas Leakage in Annulus	Insufficient hydrostatic head Gelation at cement/mud interface Failure of cement to cover gas sands Cement dehydration
Channeling	Contact of pipe with formation Poor mud properties (high plastic viscosity and high yield point) Failure to move pipe Low displacement rates Hole enlargement
Too-Rapid Setting of Cement	Improper water ratio Incorrect temperature assumption Mechanical failures Wrong cement or additives for well conditions Hot mixing water Slurry allowed to remain static to perform rig operation Improper choice of mud/cement spacers

regardless of its performance in the hardened state, it's usefulness for geothermal application is limited. Therefore, another primary purpose of the initial screening work is the desire to eliminate a large number of possible compositions which are not suitable for geothermal applications. Such preliminary screening studies accomplish this purpose with a minimum expenditure of experimental effort.

Phase I Studies: Literature Search and Personal Interviews

A thorough search of the open literature was made and several individuals considered to be experts in cementing operations were contacted.

Cementing Operations

An excellent account of the present cementing practices is given by Smith⁽¹⁾. A short review of this work encompassing primary, deep oil well and squeeze cementing techniques will suffice for our present purposes. Among the important functions of primary cementing are (1) enable effective stimulation treatments, (2) proper reservoir evaluation, (3) prevent annular communications with unwanted fluids, (4) prevent lifting of excessive well fluids, and (5) prevent accumulation of gas in the annulus. Improper cementing can also cause corrosion in the well casing. Some of the factors contributing to well failure are listed in Table 1.

The following considerations should be given to the planning and execution of a primary cementing job:

- Selection of the proper cementing material that suits the well requirements
- Bulk handling and storage facilities are very important in both economics and technical viewpoints
- "Essential volume" of water supply for mixing the cement slurry at the desired water/cement ratio, plus an allowance for pump priming, line testing, well flushing and pump cleanup

- Pumping equipment must be capable of high horsepower input and output over a wide torque limit, and yet have the lowest weight-to-power ratio for easy transportation
- Cement mixing systems should have the versatility to mix slurries of varying densities and handle different rates of mixing
- Slurry densities should be monitored and recorded continuously to insure the correct water/solids ratio
- Preflushing of the well annulus is desirable to get rid of the excess drilling mud which may have harmful effects on setting behavior of cement
- Contact time should be determined by the type of flow; for example, when the turbulent flow is attained, a contact time of 10 minutes or little longer provides excellent mud removal⁽²⁾
- Cementing wiper plugs are recommended to separate mud, cement, and displacing fluid⁽³⁾. A bottom plug is used to wipe mud from the inner walls of the casing, and to separate mud and cement. A top plug separates mud and cement and provides shutoff at the end of cementing operation
- Displacing fluids, used behind top plug, should be selected with minimum formation damage and completion time in mind
- Floation factor in big pipes
- Floation of large diameter pipes can become a problem during cementing. To deal with this problem the pipe is unclaimed and the elevators are attached to the pipe prior to pumping. As the pipe starts floating out of the hole, the pump can be slowed down. This can be done safely, since circulation is usually established by the time the pipe has risen a few feet.

Cement placement techniques are numerous depending on the needs of a particular well. Most of these techniques are modified to meet the requirement of a particular job. Among the more common cementing methods are:

- (1) Cementing through casing
- (2) Stage cementing
- (3) Inner-storring cementing through drill pipe
- (4) Outside cementing through tubing
- (5) Reverse circulation cementing
- (6) Delayed set cementing
- (7) Multiple strong cementing.

Detailed description of the above techniques can be found in references (4) through (10) at the end of this report. Figure 2 schematically illustrates various cementing techniques.

Cementing considerations for deep wells can be different as the hole conditions and working conditions encountered in deep wells are more critical and require more emphasis on casing and slurry design. These conditions would include:

- (1) Higher temperatures, higher pressures and corrosive well fluids, e.g., geothermal wells
- (2) Increased casing length, reduced annular clearances, and difficulties in moving pipe during cementing
- (3) Greater loads on the casing and drilling rig
- (4) Longer times for removing case before cementing
- (5) Heavier mud systems
- (6) Increasing differently in sealing the liner top to prevent gas or liquid communications.

All the above factors add to the difficulty and expense of deep well cementing operations.

Another type of cementing called squeeze cementing - the process of applying hydraulic pressure to force a cement slurry into a formation void or crack - is the most common type of remedial cementing. Its objective is to botain a seal between the casing and the formation to isolate the downhole water. The technical literature contains a wealth of information on squeeze cementing⁽¹¹⁻¹³⁾, still, many unconsidered questions exist:

Where does the cement go on a squeeze job?

What is formation breakdown, is it necessary?

Figure 2. Methods of placing cement down hole.

Should water or mud be used for breakdown?

Can perforations be plugged with cement?

Can the quantity of cementing be controlled during cementing?

Answers to many questions such as these remain unknown.

With a better understanding of rock fracture mechanics and filtration properties of cement slurries, squeeze cementing applications have been increased considerably. Squeeze cementing operations are used for a number of purposes⁽⁴⁻⁶⁾--

- 1) To control excessive water or gas
- 2) To repair casing leaks
- 3) To isolate unwanted fluids from the production zone
- 4) To seal off lost-circulation zones
- 5) To correct defective primary cementing jobs
- 6) To prevent fluid migration from abandoned wells.

Besides the three main cementing operations mentioned so far, a number of special cementing applications, such as large-hole cementing, waste-disposal well cementing, water-well cementing, steam-well cementing, and cementing in permafrost environments, also exist. Detailed discussions of these subjects is outside the scope of this report. Interested readers can refer to the references listed at the end of the report for further information⁽¹⁴⁻²⁰⁾.

Smith⁽¹⁾ also gives an account of the factors to be considered in cement slurry design for different applications. The following list, though not exhaustive, is representative of the parameters to be taken into account in a given cementing job:

1. Well depth
2. Well temperature
3. Mud-column pressure
4. Viscosity and water content of cement slurries
5. Pumping, or thickening, time
6. Strength of cement required to support pipe
7. Quality of available mixing water
8. Type of drilling fluid and drilling fluid additive
9. Slurry density
10. Heat of hydration
11. Permeability of set cement
12. Filtration control
13. Resistance to down-hole brines.

The importance of some of the above factors are self-explanatory; for example, pumping, or thickening time is the minimum time required to mix and pump the slurry down the hole and up the annulus behind the pipe before the viscosity of slurry gets too high to prevent its pumping. Associated with well depth are the temperature and pressure influences on cement slurries. They affect how long the slurry will pump and how well it develops the strength necessary to support pipe. Temperature has the more pronounced influence^(21, 22).

The density of a cement slurry should always be great enough to maintain well control. The density of slurries can be controlled by either controlling the type and amounts of solid materials or by controlling W/S ratios. Controlling the filtrate in the cement slurry is also very important, especially in cementing deep wells and in squeeze cementing. Loss of filtrate through a permeable medium will cause a rise in slurry viscosity, thus restricting flow during pumping.

Cementing Compositions

Considerable literature exists on the materials problems encountered in the drilling and operation of geothermal wells in terms of materials other than cements. Little has been published on actual cementing operations and cement problems in geothermal installations. A few articles⁽²³⁻²⁶⁾ mention the inadequacies of normal portland cement compositions and suggest the use of additives, e.g., silica flour and perlite, which improve the stability of cementing compositions against the severe thermal, chemical, and pressure conditions of such wells. The lack of research efforts in geothermal cements area is certainly due to the fact that geothermal resources have not been considered as alternate energy supplies until the realization of recent worldwide energy shortages.

The proceedings of the United Nations Symposium on Geothermal Resources in Pisa, Italy (1970) is probably the most substantial single scientific gathering on the subject. Even at this symposium the cementing problems, chemical compositions and thermal characteristics of various geothermal sites have been studied in conjunction with methods of extracting minerals from geothermal brines⁽²⁸⁾. Table 2 depicts elemental and mineral contents of several geothermal wells around the world.

TABLE 2. SOME GEOTHERMAL AND NONGEOTHERMAL BRINE ANALYSES,
IN ppm OF DISSOLVED IONS

Constituent	Geothermal			Non geothermal		
	Niland, Imperial	Cerro Prieto,	Wairakei,	Oilfield Brines		
	Valley, Calif.	Mexico	New	High-		
	IID No.	Well M-8	Zealand	Ocean	salinity	Low- salinity
SiO ₂	400	770	470	6.4	-	-
Al	4.2	-	-	.01	-	-
Fe	2,290	-	-	.01	-	-
Mn	1,400	-	-	.002	-	-
As	12	-	-	.003	-	-
Sb	.4	-	-	.0005	-	-
Ca	28,000	390	14	400	44,000	630
Mg	54	6	2	1,350	4,340	40
Sr	400	-	-	8.0	-	-
Ba	235	-	-	.03	-	-
Cu	8	-	-	.003	-	-
Pb	102	-	-	.00003	-	-
Zn	540	-	-	.01	-	-
Na	50,400	6,100	1,230	10,500	74,000	5,640
K	17,500	1,860	200	380	4,410	50
Li	215	17	13.5	.17	370	2
Rb	135	-	2-3	.12	-	-
Cs	14	-	2-2.5	.0005	-	-
NH ₄	409	-	-	-	-	0
HCO ₃	>150	890	46	140	95	500
SO ₄	5.4	.0	37	2,650	220	120
Cl	155,000	11,750	2,110	18,980	202,050	8,350
F	15	-	8	1.3	-	-
Br	120	14.3	-	65	5,725	70
I	18	-	-	.06	15	5
B	390	-	-	4.6	200	10
Sulfide as H ₂ S	16	-	-	-	-	-
pH (20 C)	5.2	-	-	-	-	-
T, degree C	340	-	-	-	-	-
Total	258,973	21,915	4,237.5 to 4,239.0	34,486	335,865	15,417

As Table 2 indicates these minerals may cause several problems in a geothermal installation: 1) corrosion, 2) deposition, and 3) erosion. Of the ions present Cl^- will have the most corrosive effect on the materials. Problems may also be encountered with dissolved gases, e.g., CO_2 , H_2S , etc. The corrosive action of these gases are accelerated in the presence of dissolved oxygen. Minerals such as CaCO_3 and SiO_2 cause deposition and scaling. The degree of erosion depends on the particulate matter, e.g., SiO_2 , precipitators, suspended in the geothermal waters, but entrained gas bubbles also produce significant erosive effects.

No paper has dealt with the problem of cementing and cement compositions in detail, though there has been mention of the need for improved cementing materials⁽²³⁻²⁵⁾. Matsuo⁽²⁵⁾ briefly discusses casing and cementing problems encountered in drilling for geothermal steam, specifically mentions the problem of placing the cement slurry in the well and emphasizes the importance of rheological characteristics of fresh cement slurries. The majority of cement failures are attributed to high temperatures⁽²⁴⁾ that cause radical physico-chemical changes in the cementing materials which prevent adequate solidification. Contamination of the cement with the drilling mud which remains in the annulus of the casing and well also causes failures in the performance of the cements, making the compatibility of cement slurries with the drilling mud essential.

Typical cementing compositions used in cementing geothermal wells⁽²⁷⁻²⁹⁾ have been low aluminate portland cements with 20 to 50 percent silica flour as additives along with retarders, friction reducers, and antifoaming agents, all contributing to a mixture offering some of the needed properties of pumping and rheology which are essential to the success of the operation.

Various cement slurries, gell cements, raw clay, diesel fuel bentonite, blast furnace slags, ferromanganese slags, phosphate slags have been tried as plugging cements⁽²⁹⁻³¹⁾ in numerous geothermal well sites.

It is quite evident from this brief literature search that need for improved cementing materials for geothermal applications is very real.

Phase II Studies: Initial Screening

The procedures for preparing the powdered batch and slurries and the measurements of viscosities are as follows. The powdered materials are weighed to the nearest tenth of a gram on a Metler Type P-1200 single-pan balance. Large powder batches are mixed thoroughly in a double-cone blender. Powdered mixtures so prepared are put in a Waring blender and proper quantities of water already containing the assigned admixture are added and the slurries are thoroughly mixed.

It was desired to keep the initial viscosities of slurries with different cements, additives and admixtures approximately within the same range of viscosity values. This was accomplished by simply varying the water-to-solids ratio of slurries until the desired viscosity levels were reached. Cementing compositions with bentonite and perlite as additives were the only batches which needed water-to-solids ratio of one or greater.

After mixing in the Waring blender, the slurries were poured into plastic beverage cups and the initial viscosities of the slurries were measured, employing a Brookfield Model LVT viscometer with number-3 circular disc spindle. Viscosities of some of the slurries of special interest were measured at various time intervals. The highest viscosity that can be measured with No. 3 spindle on Model LVT viscometer is 10,000 centipoises. The time at which the slurry reaches this viscosity value was taken to be the thickening time for that particular slurry. This is also an accepted description of the thickening times, as related to the pumpability, in cementing industry circles.

Upon measurement of the initial viscosities, plastic beverage cups containing cement slurries were tightly sealed with matching caps and set aside for curing at room temperature and pressure.

Thus far, more than one hundred compositions have been screened in these initial studies by measuring the initial viscosities and thickening and setting times (whenever possible). The data depicted in Tables 3 through 17 are empirical. The data are not quantitative (especially the setting times) and are quite preliminary in nature. Nonetheless, they are sufficient to provide significant implications for direction of the next stage of efforts. The materials (cements, additives and admixtures) that indicate promise already show up in these preliminary screening tests as potential candidate materials for cementing geothermal

TABLE 3. SCREENING TEST DATA FOR TYPE I PORTLAND CEMENT WITH VARIOUS ADDITIVES AND SODIUM HEXAMETAPHOSPHATE AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			μ_i	μ_t		
Type I Bentonite	1.0	0.5	2100		<24 hr	Set after 24 hr
Type I Perlite	1.0	"	500		"	"
Type I Silica Flour	0.65	"	1000		"	"
Type I Lime	0.60	"	1200		"	"
Type I Slag	0.5	"	1100		"	"
Type I Pozzolan	0.5	"	1600		"	"

* Centipoises.

TABLE 4. SCREENING TEST DATA FOR TYPE I PORTLAND CEMENT WITH VARIOUS ADDITIVES (30 PERCENT) AND CREAM OF TARTAR AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			μi	μt		
Type I Bentonite	1.0	0.5	2100			
Type I Perlite	1.0	"	400			
Type I Silica Flour	0.65	"	1000	1200 (6 hr)		
Type I Lime	1.0	"	1050	1200 (6 hr)		
Type I Slag	0.5	"	1000	1000 (6 hr)		
Type I Pozzolan	0.5	"	1350	1700 (6 hr)		

* Centipoises.

TABLE 5. SCREENING TEST DATA FOR TYPE I PORTLAND CEMENT WITH VARIOUS ADDITIVES AND (CMC) CARBOXY METHYL CELLULOSE AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities *		Thickening Time ts	Observations
			μ i	μ t		
Type I 30% Bentonite	1.0	0.5	1500	<8 hr	~36 hr	
Type I Perlite	1.125	"	700	~8 hr	~36 hr	
Type I Silica Flour	0.65	"	800	>8 hr	~36 hr	
Type I Lime	1.0	"	800	>8 hr	~36 hr	
Type I Slag	0.5	"	1700	>8 hr	~36 hr	
Type I Pozzolan	0.6	"	1400	>8 hr	~36 hr	

* Centipoises.

TABLE 6. SCREENING TEST DATA FOR TYPE III PORTLAND CEMENT WITH VARIOUS ADDITIVES AND NO ADMIXTURES

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			μ i	μ t		
Type III	0.55	0.0	1250		~3 hr	All set within 24 hr
Type III Bentonite	0.9	"	6650			
Type III Perlite	0.9	"	800		~6 hr	
Type III Silica Flour	0.5	"	1750		~6 hr	
Type III Lime	0.6	"	2100		~3 hr	
Type III Slag	0.5	"	1450		~6 hr	
Type III Pozzolan	0.55	"	1400		~6 hr	

* Centipoises.

TABLE 7. SCREENING TEST DATA FOR TYPE III PORTLAND CEMENT WITH VARIOUS ADDITIVES AND CARBOXY METHYL CELLULOSE AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities *		Thickening Time ts	Observations
			μ i	μ t		
Type III Bentonite	1.1	0.5	1700		<8 hr	All set within 24 hr
Type III Perlite	0.9	"	800		"	
Type III Silica Flour	0.5	"	1900		"	
Type III Lime	0.7	"	1250		"	
Type III Slag	0.5	"	1900		"	
Type III Pozzolan	0.55	"	2000		"	

* Centipoises.

TABLE 8. SCREENING TEST DATA FOR TYPE III PORTLAND CEMENT AND VARIOUS ADDITIVES WITH SODIUM HEXAMETAPHOSPHATE AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			μ i	μ t		
Type III Bentonite	1.15	0.5	2200		~3 hr	All set within 24 hr
Type III Perlite	0.9	"	900		<8 hr	
Type III Silica Flour	0.5	"	1150		~8 hr	
Type III Lime	0.7		2050		<8 hr	
Type III Slag	0.5		1800		~8 hr	
Type III Pozzolan	0.5		2000		~8 hr	

* Centipoises.

TABLE 9. SCREENING TEST DATA FOR TYPE V PORTLAND CEMENT AND VARIOUS ADDITIVES
WITH NO ADMIXTURES

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			μ_i	μ_t		
Type V	0.5	0.0	1200		<4 hr	Set after 8 hr
Type V Bentonite	1.5	"			<8 hr	
Type V Perlite	1.0	"	400	1300 (6 hr)	<8 hr	
Type V Silica Flour	0.5	"	1200	1200 (6 hr)	~8 hr	
Type V Lime	0.55	"	1200		<8 hr	Hard after 8 hr
Type V Slag	0.5	"	1300		~8 hr	Soft but not measurable after 8 hr
Type V Pozzolan	0.5	"	1500		<8 hr	Hard after 8 hr

* Centipoises.

TABLE 10. SCREENING TEST DATA FOR TYPE V PORTLAND CEMENT AND VARIOUS ADDITIVES (30 PERCENT) WITH CREAM OF TARTAR AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities *		Thickening Time ts	Observations
			μi	μt		
Type V Bentonite	2.1	0.5	100			Soft but not measurable after 6 hr
Type V Perlite	1.0	"	550			Not measurable after 6 hr
Type V Silica Flour	0.5	"	1350	1350 (8 hr)		
Type V Lime	0.5	"	2400			Set after 8 hr
Type V Slag	0.5	"	1600			?
Type V Pozzolan	0.5	"	2000			Set after 8 hr

* Centipoises.

TABLE 11. SCREENING TEST DATA FOR TYPE V PORTLAND CEMENT AND VARIOUS ADDITIVES (30 PERCENT) WITH CARBOXY METHYL CELLULOSE AS ADMIXTURES (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			ui	ut		
Type V Bentonite	1.0	0.5	2200	2200 (8 hr)	>8 hr	Set within 24 hr
Type V Perlite	1.3	"	1000	1000 (8 hr)	"	Set after 24 hr
Type V Silica Flour	0.5	"	1650	1650 (7 hr)	"	"
Type V Lime	0.8	"	1150	1600 (6 hr)	"	"
Type V Slag	0.6	"	1050	1250 (6 hr)	"	"
Type V Pozzolan	0.7	"	1450	1450 (6 hr)	"	Set within 24 hr

* Centipoises.

TABLE 12. SCREENING TEST DATA FOR CLASS G OILWELL CEMENT AND VARIOUS ADDITIVES
(30 PERCENT) WITH NO ADMIXTURES

Composition	W/S	Percent Admixture	Viscosities *		Thickening Time ts	Observations
			ui	ut		
Class G	0.5	0.0	800			All set within 24 hr
Class G Bentonite	1.0	"	1550			
Class G Perlite	1.15	"	300			
Class G Silica Flour	0.5	"	750			
Class G Lime	0.6	"	800			
Class G Pozzolan	0.5	"	1600			

* Centipoises.

TABLE 13. SCREENING TEST DATA FOR CLASS G OILWELL CEMENT AND VARIOUS ADDITIVES
(30 PERCENT) WITH CREAM OF TARTAR AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			ui	ut		
Class G Bentonite	1.5	0.5	Could not measure			After 18 hr not set
Class G Perlite	1.0	"	250	250 (19 hr)		Set after 36 hr
Class G Silica Flour	0.5	"	700	650 (19 hr)	>24 hr	"
Class G Lime	0.5	"	2000		<18 hr	At 20 hr soft, but not measurable
Class G Slag	0.5	"	800	700 (19 hr)	>24 hr	Set after 36 hr
Class G Pozzolan	0.5	"	900		<18 hr	At 20 hr not set, but not measurable

* Centipoises.

TABLE 14. SCREENING TEST DATA FOR CLASS G OILWELL CEMENT AND VARIOUS ADDITIVES (30 PERCENT) WITH CARBOXY METHYL CELLULOSE AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities *		Thickening Time ts	Observations
			μ i	μ t		
Class G Bentonite	1.95	0.5	3000	5500 (6 hr)	<24 hr	After 25 hr still soft-not measurable
Class G Perlite	1.0	"	900	900 (24 hr)	>24 hr	Set well beyond 48 hr
Class G Silica Flour	0.5	"	1400	1350 (24 hr)	>48 hr	"
Class G Lime	0.75	"	1600	1600 (8 hr)	>24 hr	"
Class G Slag	0.5	"	1200	1300	>48 hr	"
Class G Pozzolan	0.55	"	1500	1500 (6 hr)	>24 hr	"

* Centipoises.

TABLE 15. SCREENING TEST DATA FOR CLASS H OILWELL CEMENT AND VARIOUS ADDITIVES
(30 PERCENT) WITH NO ADMIXTURES

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			μ_i	μ_t		
Class H	0.5	0.0	700	900	~ 5 hr	Set after 24 hr
Class H Bentonite	1.0	"	2000		< 4 hr	After 6 hr not measurable
Class H Perlite	0.8	"	650		> 4 hr	Set after 24 hr
Class H Silica Flour	0.5	"	700		>12 hr	"
Class H Lime	0.55	"	1300		~12 hr	"
Class H Slag	0.5	"	1600		>12 hr	"
Class H	0.5	"	1650		~12 hr	"

* Centipoises.

TABLE 16. SCREENING TEST DATA FOR CLASS H OILWELL CEMENT AND VARIOUS ADDITIVES (30 PERCENT) WITH CARBOXY METHYL CELLULOSE AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			ui	ut		
Class H Bentonite	1.1	0.5	7950		< 4 hr	Set after 24 hr
Class H Perlite	0.9	"	650	700 (6 hr)	>12 hr	"
Class H Silica Flour	0.5	"	1400	1000 (6 hr)	>36 hr	Set after 48 hr
Class H Lime	0.6	"	1800	>1000 (6 hr)	< 6 hr	Set 36 hr
Class H Slag	0.5	"	1200	900 (6 hr)	>36 hr	Set after 48 hr
Class H Pozzolan	0.55	"	1000	1000 (6 hr)	>12 hr	Set after 36 hr

* Centipoises.

TABLE 17. SCREENING TEST DATA FOR CLASS H OILWELL CEMENT AND VARIOUS ADDITIVES (30 PERCENT) WITH SODIUM HEXAMETAPHOSPHATE AS ADMIXTURE (0.5 PERCENT)

Composition	W/S	Percent Admixture	Viscosities*		Thickening Time ts	Observations
			μi	μt		
Class H Bentonite	2.0	0.5	Could not measure			
Class H Perlite	1.0	"	600			After 24 hr still quite fluid
Class H Silica Flour	0.5	"	1100	1100 (5 hr)		All set between 36-72 hr
Class H Lime	0.5	"	2200			"
Class H Slag	0.5	"	650	650 (5 hr)		"
Class H Pozzolan	0.5	"	1650	1100 (5 hr)		"

* Centipoises.

wells. The data derived from these preliminary screening tests permit the following tentative observations:

- (1) Portland cements are not good candidate materials, especially Type I and Type III, for geothermal applications even with generous amounts of additives and admixtures in the cementing compositions. This statement is based on the setting times of pure cements - no additives and admixtures - and compositions with thirty percent additives (by weight of solids) and one-half of one percent admixture additions (by weight of solids). As can be seen from Tables 3-8, most of the cementing compositions made from Type I and Type III Portland cements set between 8 to 24 hours at room temperature and atmospheric pressure. The setting times of these cements normally change almost logarithmically with temperature (see Figure 3). A cementing composition setting in less than 24 hours at room temperature (~75 F) and atmospheric pressure would be expected to have a setting time of less than one hour at 500 F and a few hundred psi pressures. However, this general statement remains to be determined and verified experimentally, as will be in the stage III investigations.
- (2) Bentonite, perlite, and pozzolan, as examples, do not show sufficient promise as additives in potential cementing materials for geothermal applications, at least compared to silica flour and blast furnace slags. Bentonite and perlite require high W/S ratios in order to meet the initial rheological requirements (1.0 to 1.5% by weight of solids). Such high water contents in the cement slurries would be very undesirable as water loss at later stages would be high and ultimate strength would be low.
- (3) Again as a preliminary observation, it can be stated that carbocyl methyl cellulose (CMC) promises to be a very attractive

Figure 3. Effect of temperature on thickening time of various API cements at atmospheric pressure.

set retarding agent as it has shown to be superior to other admixtures (e.g., sodium hexametaphosphate, Cream of Tartar) in retarding the initial setting of cementing compositions examined thus far. Before one can make more concrete conclusions as to the effectiveness of CMC, however, the high temperature thermal - chemical stability of this compound will have to be tested in the Phase III studies.

These then represent a few cautious observations that can be made from the limited data obtained thus far. However, before the most promising cementing compositions can be selected for the Phase III, high temperature and pressure rheological studies, and additional large number of possible compositions remain to be studied in the initial screening phase. The initial screening experiments will be continued on remaining possible combinations of materials listed in Table 1.

After the initial screening tests have been completed, a representative number of compositions will be subjected to rigorous high temperature and pressure rheological tests as previously described.

FUTURE WORK

A number of cement, additive and admixture combinations remain to be studied in the initial screening efforts. Attention will be directed toward completion of the initial screening studies. After the initial screening tests have been completed, a number of selected compositions will be evaluated for autoclave curing characteristics in the Phase III studies, where thickening and setting times will be determined at 400 to 500 F temperature range and steam pressures at these temperatures. The property determination of the compositions cured under the conditions of geothermal environment as simulated by laboratory autoclave curing will proceed the Phase III work on autoclave curing characteristics.

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APPENDIX 4

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

A report to:

Brookhaven National Laboratory
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for:

Contract No. 422272-S

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December 15, 1977

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

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

A. Introduction

The object of this research is to prepare new high temperature cementing materials for geothermal wells utilizing compositions in the systems $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and possible intermediate mixtures. The cements will be tested for long term strength, permeability, bond strength, and stability under high temperature, high pressure, and brine contact. Within both systems both gel starting materials and commercial cements (with added oxides) are being prepared. Initially the gels, in sealed gold tubes, are being treated hydrothermally at 5000 to 10,000 psi (34,500 to 69,000 kPa) and 200 to 400°C. The commercial cement pastes, prepared as 2 to 2.5 cm diameter cylinders, are being treated hydrothermally in autoclaves at 1500 to 10,000 psi (10,300 to 69,000 kPa) and 150 to 400°C. Initial results from short duration experiments (about 50 hours) indicate that the gel compositions are more reactive than the cement-oxide mixtures under the conditions being investigated and are likely to be of considerable value in the determination of the stable phase relationships in the temperature and pressure ranges of interest. These also indicate that intermediate or metastable phases develop before stable equilibrium is attained and that previously unidentified phases may be encountered.

Commercial cements being used (along with added oxides) include Unadeep cement, Fondu cement, Secar cement, and Refcon. Fine quartz "Minusil" (5 μm size) was used as the source of silica. X-ray diffraction for phase analysis, microhardness (correlated to compressive strength), and permeability are the primary measurements made to date.

B. Experiments with Stock Chemical Starting Materials

An experimental preparation was made with MgO and CaO stock chemicals combined with 5 μm "Minusil" SiO_2 . The mixture was 10% MgO, 40% CaO, and 50% SiO_2 , and 46% H_2O . Cylindrical samples of this composition injected into a mold had numerous air pockets whereas samples inserted along the mold

had a negligible number of air pockets. After curing the samples for 24 hours at 100% relative humidity, further hydrothermal curing for 50 hours at 400°C and 2000 psi (13,800 kPa) caused the cylinders to disintegrate. X-ray analysis of the ooze at the bottom of the autoclave indicated that the dominant phase was killalaite $2\text{Ca}_3\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$. Though the starting materials were relatively reactive, the loss in strength indicates there is no point in further work with only stock chemicals. Future starting materials for cylinder preparation will employ dominantly commercial preparations.

C. Experiments with Gel Starting Materials

1. Preparation

In order to optimize the reactivity and homogeneity of the required reactants gel preparations were used. The desired quantities of Mg^{2+} and Ca^{2+} are added individually as aqueous solutions of the nitrates $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ to the appropriate volume of colloidal silica (Ludox) in the MgO-CaO-SiO_2 system. In the $\text{Al}_2\text{O}_3\text{-CaO-SiO}_2$ system Al^{3+} is added individually as an aqueous solution of the nitrate $\text{Al}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$. After thorough stirring to ensure homogeneity of the mixed solutions, the Ludox was hydrolysed by the addition of sufficient NH_4OH solution. The resulting precipitated gel was evaporated slowly for several hours and then ignited at the minimum temperature necessary to decompose the nitrate. The temperature of ignition is minimized to avoid crystallization of the amorphous material. The resulting amorphous solid was crushed to a fine powder and checked by diffractometry and optical microscopy to ensure the absence of crystalline phases.

2. Hydrothermal experiments

Gel compositions within the $\text{MgO-CaO-SiO}_2\text{-H}_2\text{O}$ system are shown in Fig. 1; those within the $\text{Al}_2\text{O}_3\text{-CaO-SiO}_2\text{-H}_2\text{O}$ system are shown in Fig. 2. A variety of temperature and pressure conditions will be investigated but initially compound formations and phase equilibrium studies were carried out at 300 to 400°C and 5000 to 15,000 psi (34,500 to 103,500 kPa). Where necessary the compositions being studied correspond to the cement compositions being investigated under similar hydrothermal conditions.

Accurately weighed quantities of the amorphous solids (approximately

Figure 1. Gel and cement mixtures used for hydro-thermal runs in the MgO-CaO-SiO₂-H₂O system.

Figure 2. Gel and cement mixtures used for hydrothermal runs in the Al₂O₃-CaO-SiO₂-H₂O system.

0.25 grams) and distilled water (weight ratio 1:1) were treated hydrothermally in sealed 5 mm gold tubes. These tubes were sealed carefully by small welds and weighed accurately before and after hydrothermal treatment.

Identification and characterization of reaction products was achieved by x-ray diffraction and optical examination of the reacted material. At present these experiments indicate that while the gel preparations appear to be sufficiently reactive under the conditions being investigated, reaction is in all cases incomplete and experiments of substantially longer duration (possibly several weeks) are required before stable equilibrium can be attained. Hydrothermal experiments over longer time intervals are now being undertaken with a view to determining the stable phase relationships. Where necessary these studies will be supplemented by other experiments, designed to ensure stable phase equilibrium using other materials as starting reactants.

In the Al_2O_3 system the join $\text{CaO} \cdot \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ was chosen for the initial investigation in order to become familiar with the hydrothermal equipment and with the reacted materials. In 1960 a portion of the quaternary system, the join $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{SiO}_2 - \text{H}_2\text{O}$ had been investigated by Koizumi and Roy in a determination of the phase relationships for calcium zeolites as shown in Fig. 3. Koizumi and Roy also studied the equilibrium relationships in the zone labeled aluminous cements and determined the stability limits and structure for a number of minerals and synthetic phases in this quaternary system as shown in Fig. 4. In addition, there is a quaternary series of hydrogarnets extending from hydrogrossularite.

D. Experiments with Commercial Cements as Starting Materials

1. Preparation

Commercial cements being used (along with added oxides) include Unadeep cement, Fondu cement, Secar cement, and Refcon. Thus far only Unadeep and Secar cements have been used in the $\text{CaO} - \text{MgO} - \text{SiO}_2$ and $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ systems respectively. Fine grained quartz "Minusil" (5 μm size) has been used as the source of silica.

A mixture of Unadeep with 10 percent MgO produced a product similar chemically to the stock chemical sample mentioned in Section A. This mix

Figure 3. Compositions of interest in the Al₂O₃-CaO-SiO₂-H₂O system.

Figure 4. P-t diagram showing probable phase assemblages stable in divariant p-t regions and univariant p-t curves separating such regions (after Koizumi and Roy, 1960).

is shown in Fig. 1 as #2¹¹. Distilled water was mixed with this cement using a 0.46 water/cement ratio. The w/c ratio was kept to a minimum while allowing maximum workability. These samples were first cured at room temperature for 24 hours at 100 percent humidity before hydrothermal treatment.

Sample #3¹¹ in Fig. 1 is a mixture of Unadeep plus MgO and CaO to produce a mixture of 50% SiO₂, 25% MgO, and 25% CaO. Some of this sample was cured for about 96 hours while other of this sample was cured for 24 hours. The longer cured samples were much more stable reflecting the slow curing of the Unadeep cement.

A mixture of Secar cement with 50% 5 μ m "Minusil" SiO₂ was treated under two different hydrothermal conditions. The composition of this mixture with a 0.4 w/c ratio is shown in Fig. 2 as #1S. These samples were cured overnight at 100% relative humidity at room temperature.

2. Hydrothermal experiments

The hydrothermal experiments were made in high pressure autoclaves designed for a maximum pressure of 15,000 psi (103,500 kPa) at 600°C with a safety factor of 3. For the Secar-cement hydrothermal experiments the furnaces were preheated before the autoclave was inserted; for the Unadeep cement hydrothermal experiments the furnace was heated slowly or adjusted to the final operating temperature when the autoclave was inserted.

The heating curves, temperature vs. time, for a furnace temperature setting of 600°C is shown in Fig. 5. This gives the actual temperature of the furnace, the temperature at the bottom outside of the autoclave, 2 inches above the bottom outside, and at the bottom inside of the autoclave. The furnace temperature reached the final temperature of 630°C after 3 hours. At the equilibrium temperature and pressure after 6 hours the outside temperature at the bottom was 530°C; outside 2 inches above the bottom was 500°C; and inside at the bottom was 400°C. If the furnace temperature was lowered the autoclave outside and inside temperature equilibrated (within 1 hour) and both cooled very slowly over 15 hours to 55°C.

3. Properties

Samples of the cement pastes must be prepared for the property measurements therefore some of these procedures are outlined below.

Figure 5. Heating curves for autoclave.

a. Microhardness

Samples were sawed to an appropriate size for easy handling (about 1 cm thick) and to have parallel edges. The samples were then ground using #3 Alumina powder and water on a smooth glass surface. The surface of the sample was then polished to a glassy shine using a 1-micron size diamond paste until enough surface area was present to make the microhardness tests. All the polishing was done in a nitrogen atmosphere to reduce sample reaction. Vickers microhardness is measured using a 400X objective.

b. Compressive strength

Prior to compressive strength testing of the sample, it was sawed on both ends, lightly sanded and returned to a curing solution of saturated Ca(OH)_2 . A Tinius Olsen Testing Machine was used for this test with a loading rate of 0.2 inches (0.05 mm) per minute. The sample was removed from the curing solution and blotted dry just prior to testing and the data were recorded from the 12,000 lb (5400 kg) scale. A square of paper was placed between each end of the sample and the machine platens to fill any voids in the surface of the sample and to protect the equipment.

c. Permeability

The sample used for permeability measurements was blotted dry after the hydrothermal curing then placed in a desiccator containing drierite and ascarite. Just before the permeability was measured the sample was dried at 110°C for 1 hour.

d. Other property measurements

Other property measurements include using the scanning electron microscope and measurement of the thermal gradient.

E. Results

The hydrothermal experiments which have been carried out to date, although of short duration and on a limited number of compositions, indicate that in the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ system the compounds, talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$; sepiolite, $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$; anthophyllite, $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$; and brucite, $\text{Mg}(\text{OH})_2$ from gel starting materials and killalaite, $2\text{Ca}_3\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$ and xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ from Unadeep cement starting material may be the important

TABLE 1

Sample	Temp. (°C)	Pressure (psi)	Initial Condition	Hydrothermal Curing (days)	Resulting Phases
1	400	10,000	gel	7	Anorthite + ?
2	400	10,000	gel	7	Phase X + boehmite + prehnite + ?
3	400	10,000	gel	7	Phase X + boehmite + ?
1S	400	1400	cement	3	Phase X + boehmite + quartz
2S	325	1400	cement	6	Phase X + wairakite + quartz

Permeability of sample #1S is 1.36×10^{-5} Darcys extrapolated for H₂O permeability, as shown in Fig. 6.

phases. Some or all of these phases may have regions of stability under the conditions investigated.

These same experiments indicate that stable equilibrium is attained only slowly and that hydrothermal treatment of the compositions under study of much longer duration will be necessary to establish the stable phase equilibrium over a wider range of compositions and hydrothermal conditions.

Cement compositions using Secar cement have been treated hydrothermally at 400°C at 1400 psi (9750 kPa) for 3 days. Three crystalline phases were present: Phase X + quartz (SiO₂) + boehmite AlO(OH). If the same mixture of Secar cement with 50% "Minusil" was hydrothermally treated at 325°C at 1400 psi for 6 days then the resulting crystalline phases are phase X + quartz (SiO₂) + wairakite (CaAl₂Si₄O₂·2H₂O). The second experimental run had a cement sample still in a glass bottle included. The glass had re-crystallized and the surfaces were coated with tiny crystals of wairakite. The sample texture was quite different between the first and second runs.

Within the system Al₂O₃-CaO-SiO₂-H₂O the results are shown in Table 1.

Figure 6. Permeability of Sample #1S.

Personnel

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

APPENDIX 5

SOUTHWEST RESEARCH INSTITUTE

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HIGH-TEMPERATURE CEMENT FOR GEOTHERMAL WELLS

TECHNICAL PROGRESS REPORT NO. 1

October - December 1977

SwRI Project 02-5083

to

Brookhaven National Laboratory
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APPROVED:

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ABSTRACT

A program for the development of a high-temperature geothermal-well cement was started October 1, 1977. In the first quarter, a review was made of the literature on geothermal-well cements, oil- and gas-well cements, and hydrothermal cements. Research on Southwest Research Institute's hydrothermal cement formulation has been ongoing to develop pumping capabilities above 425°F. Work accomplished during the period October 1, 1977, through December 31, 1977, is described in this first technical progress report.

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I. INTRODUCTION

Southwest Research Institute (SwRI) has begun a research program to develop an improved cement for use in high-temperature geothermal wells. This report describes research carried out during the first quarter of Brookhaven National Laboratory Contract No. 427964-S.

During the period of October 1 to December 31, 1977, a review was made of background data including published material and SwRI data. Evaluation of a considerable amount of collected information, dating from 1970, was made. A number of SwRI cement formulations were examined, preliminary screenings were made, and physical testing was performed to determine suitability of the particular cement for use at 450°F (232°C). Cement formulations curing at 600°F (316°C) were examined, and several were selected for further screening.

II. LITERATURE REVIEW AND EVALUATION

Abstracts of over a thousand references pertaining to geothermal-well cements, oil/gas-well cements, hydrothermal cements, and well completions were examined. Of these, 78 were considered pertinent to this program, and copies of these articles and documents were obtained for review.

A. General Information

The cementing of casing in any well, whether for producing hydrocarbons or for production of geothermal steam, is almost a universal practice. A number of geothermal wells are produced open-hole. However, as use of geothermal steam power increases and more and more production wells are drilled, cementing of at least some of the hole will be required. As the temperatures of the producing zones increase to 200 to 300°C, completion of the well will require that the casing be effectively cemented to the formation. In the very high-temperature geothermal wells and deep geopressured wells it will be mandatory to have production strings cemented to withstand high temperatures, high pressures and highly corrosive fluids existing under these conditions.

As an aid to those not familiar with well completion and cementing techniques and problems, the following literature survey was made. As mentioned above, most of the oil/gas well technology is applicable to geothermal well completions.

If an overview of the field of geothermal energy is desired, a number of documents have been published which provide the information. Kruger and Ott^{(1)*} give some information on just about all phases of geothermal power. However, there is nothing in this book on the completion of wells. A source document

* Superscript numbers refer to references listed in Section IV, "Bibliography."

of the National Technical Information Service by Smith⁽²⁾ provides a continuing bibliography of all government-sponsored research on geothermal energy. One of the most ambitious documents is the ERDA bibliography on geothermal resources.⁽³⁾ This is a comprehensive bibliography containing 5,476 citations of foreign and domestic research reports, journal articles, patents, conference proceedings, and books concerned with the exploration and exploitation of geothermal resources. The coverage dates back as far as useful references could be obtained and extends through June 1976. This is a valuable addition to the geothermal library .

Various proceedings volumes (4,5) and workshops⁽⁶⁾ cover a wide range of subject matter on geothermal energy, including the various geological sciences, drilling and production technology, energy utilization, environmental engineering, economics, and law. Many foreign authors are included, giving some information concerning geothermal developments in Italy, Mexico, Iceland, and other important areas. Armstead⁽⁷⁾ has brought together a number of excellent articles on geothermal energy.

B. Cements

The cementing of geothermal wells may be the most important operation in the completion process. Surface casing must be cemented in order to seal off and protect freshwater formations, provide an anchor for surface equipment, and give support at the surface for the deeper strings of casing. Intermediate strings of casing are cemented in order to seal off abnormal pressure formations effectively, isolate incompetent formations which would cause excessive sloughing unless supported by casing and cement, and shut off zones of lost circulation to prevent migration of fluids or steam to thief zones. Cement also effectively protects the casing from corrosive environments, notably corrosive fluids.

The cementing programs used in geothermal wells are usually similar to those used in deep oil or gas wells with high bottom-hole temperatures. An estimate has been made by Jet Propulsion Laboratory⁽⁸⁾ indicating a need for about 5,000 production, and 2,000 reinjection, wells to provide a national goal of 20,000 MW electrical power by 1985. If these wells require about 600 ft of very high-temperature cementing, an estimated 150 sacks of special cement would be used for each well. Total cement requirements for the 7,000 wells, with an average depth of 5,000 ft, would be well over 12 million sacks of cement. Volumes were calculated from theoretical rheology of an average hole, according to Graham.⁽⁹⁾

The American Society for Testing Materials (ASTM) has adopted specifications for ten different types of portland cements.⁽¹⁰⁾ However, these do not adequately define the properties required in oil and gas, or geothermal, wells. Therefore, the American Petroleum Institute (API) has established specifications for nine classes of oil-well cement.⁽¹¹⁾ These specifications have been accepted for cements for use in geothermal wells. The API specifications do not specify portland cement, but they do specify the chemical requirements of each type of cement.

Working with well cements requires some knowledge of the nomenclature. API has defined the most commonly used terms associated with oil-well cementing⁽¹²⁾, also applicable to geothermal-well cementing.

For testing of oil- and geothermal-well cements and cement additives, the standard is the API RP10B.⁽¹³⁾ Within the sections on each test, many of the ASTM standard tests are used. The purpose of this publication is to define the mandatory tests in Paragraph 2.6 of Specification 10A, and the nonmandatory tests for evaluating the physical properties of cements. New cement test schedules are issued as deeper and hotter wells are being drilled.

A brief but comprehensive overview of cements and well-cementing has been written by Parker, Clement and Beirute as an eight-part series on basic cementing. The series includes cement manufacture⁽¹⁴⁾, specialty cements⁽¹⁵⁾, additives and their application⁽¹⁶⁾, slurry design⁽¹⁷⁾, how to cement casing⁽¹⁸⁾, squeezing and plugging⁽¹⁹⁾, cementing calculations⁽²⁰⁾, and auxiliary equipment and materials.⁽²¹⁾

A similar overview of the cementing of wells is an eight-part series by Suman and Ellis. This series includes basic functions of cement⁽²²⁾, casing handling and inspection⁽²³⁾, cement slurry chemistry and use of additives⁽²⁴⁾, displacement mechanics and rheology⁽²⁵⁾, guidelines for down-hole equipment and primary cementing techniques⁽²⁶⁾, liner cementing, techniques and problems of pumping and placing cement⁽²⁷⁾, special cementing such as plugging, squeezing and tubingless completions⁽²⁸⁾, and methods for evaluating primary cementing effectiveness.⁽²⁹⁾ These two series are both timely and excellent summaries of the whole spectrum of well cementing.

Portland cements, modified with various additives, make up the bulk of presently used geothermal-well cements. Recently, a number of new, nonportland cements have been developed and give promise of being good high-temperature cements.

Aldrich⁽³⁰⁾ describes an API Class G cement mixed with an additive to give a foamed, cellular cement. He claims it has practical compressive strength, high permeability or low permeability depending on porosity, and has a future where light densities are required.

Cigni, et al⁽³¹⁾, discuss the cements used in Italian geothermal fields where temperatures have been encountered up to 300°C. Problems are found mostly in the lower string of cemented casing, caused by thermal conditions. They have

had reasonable success with a mix of 100 parts portland, 40 parts silica flour and retarders. They mention some test variances caused by using simulated conditions not totally representative of true down-hole conditions.

Clark, et al⁽³²⁾, discuss tests made on a Class H cement developed by removing fines from the cement powder. This cement shows an increased thickening time which makes the slurry useful for high-temperature well cementing. The slurries showed high compressive strength, low permeability, and acceptable free-water loss.

Eilers, et al⁽³³⁾, report on the development of geothermal-well completion systems. This, of course, is a part of the DOE/Brookhaven research program to find good high-temperature cements. The authors gathered information from companies experienced in geothermal-well cementing concerning problems expected and cement requirements. The report also described Dowell's current high-temperature cement research.

Kalousek and Chaw⁽³⁴⁾ discuss research relating some of the indicated low strengths of hot-well cements to the lime/silica ratio and the amount of alumina. Optimum compositions and ratios were presented. Six hydrated calcium silicates were found as potential binders in the study. The effect of alumina, ranging from beneficial to deleterious, was determined.

Kukacka, et al⁽³⁵⁾, have been involved in a long-term research program to determine the state-of-the-art and the potential for new geothermal-well cementing materials. Also, they are selecting and evaluating polymer cements. Research contracts for the development of high-temperature inorganic materials have been awarded to five research organizations. This research encompasses almost every conceivable cement system.

Mallow and Dean⁽³⁶⁾ presented a novel hydrothermal cement consisting of alkali metal silicates, polyvalent metal ions, siliceous fillers, and a hydratable silica source. These cements have a large number of unique chemical and physical properties. Of particular importance is the ability to retain their mobility and pumpability at high temperatures, up to 425°F and increments of that, according to the recipe.

Maravilla⁽³⁷⁾ presented laboratory data to show that a unique hydrothermal setting cement can be used as manufactured--without the addition of high-temperature retarders--to cement oil and gas wells (and geothermal) where bottom-hole static temperature is in the range of 260 to 320°F. Retarders and other additives can be used to extend that range. This cement is composed of a binder, quartz sand, and calcium hydroxide. The binder is beta dicalcium silicate, one of the main mineral constituents of portland cement. It is considered an API Class J cement with good physical performance statistics.

Tschirley⁽³⁸⁾ discussed problems encountered in deep, hot wells with bottom-hole temperatures of 500°F and beyond. Laboratory tests proved that interface thickening of high-density oil muds and cements can be prevented by using the proper spacer fluid and circulating to cool down the bottom section of the well before cementing.

C. Effects of Temperature and Pressure

Field engineers and others who handle cementing for present-day wells are responsible for one of the most critical phases of well completion. It has never been so important from the standpoint of safety, environmental protection, and economics to insist that the best available technology be applied.

One of the most important factors controlling the chemical reaction, and the resultant performance, of a cementing composition is the temperature to which it is exposed. Tregesser and Parker⁽³⁹⁾ outlined in 1972 the many problems to be encountered in deep, hot, or just hot, wells. Accurate field measurements of well temperatures will be a requirement when cementing wells that have temperatures of up to 300°C.

Temperature and pressure were recognized as the primary problems in deep and ultrahot wells. Phillips and Sykes⁽⁴⁰⁾ and Holmes and Swift⁽⁴¹⁾ recognized these problems and suggest methods which can improve well cementing under high-temperature conditions. It is suggested that 800°F may be the highest temperature to be expected, even under abnormal geothermal gradients. Except for very deep wells, i.e., greater than 20,000 ft, most geothermal wells usually have a lower than normal pressure gradient.

Beyond the problems encountered with high temperatures controlling the setting of the cement, variable formation temperatures above the producing zone may have to be reckoned with. McNitt⁽⁴²⁾ suggests that temperature logs be run during drilling so that the variations will be known. So-called cold zones may actually be so cold that they inhibit the cement from setting.

Bottom-hole temperature in an oil well is the most important factor affecting the choice of oil-well cement according to Shell and Tregesser.⁽⁴³⁾ This is also true of geothermal wells. Temperature information is also useful in other phases of drilling, completing and producing wells. This paper presents the results of the gathering of such temperatures by a task group of the API Committee on Standardization of Oil-Well Cements.

Boone⁽⁴⁴⁾ discusses effective cementing and analyzes the effect of hydrostatic pressure of cement and mud on the cementing operation. If internal

pressure is maintained on the casing during cement cure, the casing will pull away from the cement when pressure is released.

D. Strength of Cement (Compressive and Bond)

Adequate cement strength has been commented on in many of the previous references. In this section, several papers will be mentioned which are concerned specifically with the compressive and bond strengths of well cements.

Boone⁽⁴⁵⁾ discusses the loading of cement by hydrostatic forces. Many cementing failures are caused by not taking into account the various pressures working on the cement during curing. He suggests that the cement have a compressive strength equal to the maximum anticipated differential pressure between the original formation pressure, in a zone above or below, and the minimum pressure reached in producing the reservoir.

Smith⁽⁴⁶⁾ suggests that the minimum strength required for proper operation of a well is thought to be about 3500 kPa (507 psi).

Fertl, et al⁽⁴⁷⁾, review cement bond logs as to how they are interpreted and what information is obtainable with them. He discusses pitfalls, misinterpreted logs, and proper techniques to use. If used properly, they are a valuable tool for evaluating the bond of the cement to both the casing and the formation.

E. Porosity, Permeability, and Stability of Cements

These factors are dealt with in many of the previous references. Cook and Cunningham⁽⁴⁸⁾ stress that recent studies have illustrated the need for filtrate-loss controlled cementing slurries to aid in the prevention of fluids leakage following primary and liner cementing. Christian, et al⁽⁴⁹⁾, also show that fluid-loss additives are important for controlling or preventing gas/fluids migration.

The stability of cements under actual well conditions is discussed by Beirute and Tragesser.⁽⁵⁰⁾ The expansive and shrinkage characteristics of well cements under actual well conditions of temperature and pressure have been measured by a highly sensitive device especially developed for the purpose. It was learned that some cements first shrink during the initial set of the cement.

F. Cementing Methods

Cementing methods are numerous and variable. Each well will be cemented according to the well conditioning, depth, temperature, pressure, mud system, and other requirements. Determination of a particular cement and method should be chosen with great care and by using all possible knowledge of the existing conditions.

Graham⁽⁹⁾ gives a well-written account of a rheology-balanced cementing method with many mud and cement curves and formulas for predicting the best combinations of cement flow factors, pumping rates, etc., to perform the best possible well-cementing job. One of the best books on well cementing is by Smith.⁽⁴⁶⁾ This book presents a composite review of the technical literature on well cementing. Basic principles, materials, and techniques of cementing are reviewed and illustrated.

After selection of the system and method, a spacer fluid is usually placed ahead of the cement. It is most important to insure the cleanest possible conditions at the surfaces to be cemented. Matsuo⁽⁵¹⁾ suggests maintaining a low filter-cake mud system to avoid severe cleaning problems. Beirute⁽⁵²⁾, Carney^(53,54,55), Clark and Carter⁽⁵⁶⁾, and Garvin and Slagle⁽⁵⁷⁾ discuss a number of spacer fluids which may be used under various conditions.

Beirute's paper deals with the problem of formation damage and use of his spacer system to clean the casing and well-bore surfaces to provide the best cement bond strength. Carney describes the development of several spacer fluids that are compatible with the cement slurries. Clark and Carter describe a test facility for determining the forces available and involved in displacing the mud with a cement slurry. Garvin and Slagle discuss tests conducted in model well-bores to determine the influence of relative mud-cement weights and yield values upon displacement efficiency.

Braunlich⁽⁵⁸⁾ discusses several well-completion techniques used by the oil industry. Three main stages in the well completion operations are featured: cementing, perforating, and stimulation.

Running and cementing deep liners are explained by Lindsey.^(59,60) It is important that good clean-out procedures are closely followed. Significant components that are used in setting the liners are described and illustrated.

Poblano⁽⁶¹⁾ describes a computer method for calculating the proper type of cement and additives required for a particular cement job. Computers are utilized to consider the effects of many variables on the displacement efficiency of casing slurries. A flow chart of the program used is provided. Its logic is to test first for the turbulent flow method, then laminar flow and, finally, the stage method. Results of over 50 cementing jobs were good.

G. Cement Failures and Repairs

There are many reasons for cementing casing in the well-bore. Among the most important are: (a) it provides vertical and radial support to the casing string; (b) it permits control of the well if further drilling is done;

(c) it protects the casing from corrosion; (d) it isolates porous formations to prevent migration of fluids and gases; and (e) it facilitates selective well treatment.

Problems encountered during and after primary cementations generally can be traced back to an incomplete displacement of the drilling fluids by the cement slurry. The result is an inadequate annular seal due to lack of bonding to both the casing and the formation. After cementing is complete, a cement bond log or temperature survey should be run. If gaps are found between casing and formation or casing and hardened cement in a critical zone, squeeze cementing should be considered. Where high pressure and temperature do exist, casing failures can occur where incomplete cementing has been found. Murphy⁽⁶²⁾ describes several techniques for recement jobs in zones of faulty primary cementing.

At Cerro Prieto, Mexico, failures were observed in all wells where casings were used as production casing and, at the same time, as mechanical support of the bore-hole walls.⁽⁶³⁾ Construction deficiencies and the use of standard cement aggravated the problems and increased the number of collapses and fractures. Factors which, together with thermal effects, caused problems are:

- ° Reservoir temperature levels from 250 to 345°C.
- ° Faulty well drilling features, frozen casings, cement channeling and using only one casing for wall support and production, as mentioned above.
- ° Failures were caused by incrustations, corrosion, collapses, fractures of cement, sand invasion, and loss of control.

Repairs were usually made by injecting grout at 400 to 600 psi in collapsed or channeled cement. Casing had to be cemented along the total length using modified Type G cement with silica and perlite.

High-strength steel casings had to be used to withstand the tensile stresses, compressive stresses, and collapsing pressures, which were much more than in oil or gas wells because of the thermal effect.

It is necessary to give thorough study to well conditions in order to achieve satisfactory squeeze cementing jobs, according to Boone.⁽⁶⁴⁾ Squeeze cementing is a complex combination of fracturing, filtration rate, bonding, cement strength and chemistry.

Rike⁽⁶⁵⁾ discusses the use of squeeze cementing to exclude water, gas, or oil from the producing formation, repair of casing or pipe failure, and repair of a faulty primary cement job. The paper describes the low-pressure squeeze, extenders and fluid-loss control, retarders, etc., as well as special cement systems.

H. Drilling Geothermal Wells

Drilling and completing geothermal wells is not too much different than conventional oil field wells. Several good reports explain how geothermal wells are typically drilled and completed, particularly in the Imperial Valley and the Geysers areas of California.

The differences between drilling a geothermal well and an oil well are discussed by Cromling.⁽⁶⁶⁾ The high temperatures associated with geothermal wells affect the circulating system and the cementing procedures, as well as the design of casing and drilling string. These unique problems must be coped with along with those normally encountered. This paper describes drilling in the Geysers area and Imperial Valley.

Cromling's second article⁽⁶⁷⁾ duplicates much of the above, while adding a few notes concerning the use of blow-out preventers on geothermal wells.

Matsuo⁽⁵⁾ gives a good report on drilling for geothermal steam and hot water. He rates drilling rigs, and discusses methods and mud systems, cementing of wells, and numerous other facets of geothermal well drilling and completion.

To complete this section, several documents on drilling fluids are included. The Bureau of Mines has made an extensive literature survey on geothermal-well drilling fluid technology.⁽⁶⁸⁾ This paper describes the composition, properties, and problems encountered with drilling fluids of various formulations used at the important geothermal areas of the world.

API Bulletin D11⁽⁶⁹⁾ is a glossary of drilling-fluid and associated terms, and API Bulletin D4 reports on the effects of drilling-mud additives on oil-well cements.⁽⁷⁰⁾

I. Miscellaneous

There are a great many more references available concerning geothermal wells, including the drilling of wells, mechanics of geothermal fluids or steam, and various aspects of well completion, especially if one goes back prior to 1970. Most of the references included in this report contain bibliographies or reference lists of from several to more than 50 articles, much of it pre-1970.

The following are some of the miscellaneous articles of interest. While they are not directly related to geothermal cements and cementing, they are concerned with some of the problems which may be found in the geothermal environment and provide general information on the deep geopressured zones which will be produced in the future.

An "Assessment of Geothermal Resources"⁽⁷¹⁾ lists many of the geothermal areas of the U.S. by various characteristics.

DePuy, et al⁽⁷²⁾, and Kukacka, et al⁽⁷³⁾, are concerned with research on polymer-concrete composites for energy-related systems. These materials are needed for handling hot brine and steam. Thermal and physical properties of these materials are being studied.

The last five articles and documents reviewed are concerned with geopressured geothermal resources. Authors of the various papers are Bebout and Gregory⁽⁷⁴⁾, Dorfman and Deller⁽⁷⁵⁾, Howard, et al⁽⁷⁶⁾, Swanson, et al⁽⁷⁷⁾, and Wilson, et al.⁽⁷⁸⁾

Most down-hole equipment for use on both conventional oil field and geothermal wells are efficient up to about 500°F. Cementing tools and, of course, the well casing itself, will need to withstand even higher temperatures in the future. Research is going on to develop improved down-hole equipment. We are developing the new cements for use at these high temperatures; it is also going to take new materials to put the cement down into the hole.

Steels used in drilling and producing oil and gas wells are also used in geothermal wells. These steels may lose much of their strength when they are exposed to temperatures in excess of 500°F. The thermal expansion of steel is much greater than cement at these temperatures. Several strings of casings are usually required in geothermal wells in order to control formation fluids and to prevent excessive loss of formation into the well-bore. Cementing in most very hot geothermal wells must be from the surface to the producing formation and, in the future, in the hot production zone. Therefore, new materials will be needed to be compatible with the high temperatures.

III. SWRI SILICA POLYMER CEMENT

A. Formulations

The basic recipes, as stated in Reference 36, have been modified by the addition of several ingredients. These include alumina, zirconia, and zinc oxide; others will be tried. Additions of zirconia have increased the useful pumping temperatures to over 500°F.

B. Initial Physical Testing

Consistometric tests have been made on the 450°F cement formulations with success. These cements can be pumped for more than four hours with little thickening. Formulations for use at 600°F have not yet been successful on consistometric tests.

C. Administrative

During the current report period, three "Monthly Administrative Letters" were submitted to Brookhaven National Laboratory.

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