BNL 33127
INFORMAL REPORT

HIGH-TEMPERATURE CEMENTING MATERIALS FOR
COMPLETION OF GEOTHERMAL WELLS

FINAL REPORT

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on

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COMPLETION OF GEOTHERMAL WELLS

to

Brookhaven National Laboratory
Associated Universities, Inc.

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ABSTRACT

A research program, aimed at developing high-temperature cementing materials for geothermal well completions, was undertaken under a contract from Brookhaven National Laboratory (BNL).

Several portland cement types, oil well cements, and various additives and admixtures were evaluated during the course of development of a number of promising compositions suitable for geothermal applications. Among the cements and various materials considered were portland cement Types I, III, and V; oil well cement Classes G, H, and J; and additives such as silica flour, blast furnace slags, pozzolan, hydrated lime, per-lite, and aluminum phosphate.

Properties of interest in the study were thickening time, compressive strength, cement-to-metal bond strength, and effects of the cements on the corrosion of steel well casings.

Testing procedures and property data obtained on a number of compositions are presented and discussed.

Several cementing compositions comprised of Class J oil well cement, pozzolan, blast furnace slags, and silica flour were found to possess properties which appear to make them suitable for use in geothermal well completions.

Five of the promising cementing compositions have been submitted to the National Bureau of Standards for additional testing.

NOMENCLATURE

I	- Type I Portland Cement
III	- Type III Portland Cement
V	- Type V Portland Cement
G	- Class G Oil Well Cement
H	- Class H Oil Well Cement
J	- Class J Oil Well Cement
SF	- Silica Flour
HL	- Hydrated Lime
BFS	- Blast Furnace Slag
AP	- Aluminum Phosphate
PT	- Perlite
P	- Pozzolan
CMC	- Carboxy Methyl Cellulose
CMHEC	- Carboxy Methyl Hydroxy Ethyl Cellulose
CT	- Cream of Tartar
CAL	- Calgon
BA	- Boric Acid
t _T	- Thickening Time
t _s	- Setting Time
W/C	- Water-to-Solids Ratio
Uc	- Units of Consistency

HIGH-TEMPERATURE CEMENTING MATERIALS
FOR COMPLETION OF GEOTHERMAL WELLS

FINAL REPORT

BATTELLE
Columbus Laboratories

1. EXECUTIVE SUMMARY

A laboratory research program to develop high-temperature cementing materials for the completion of geothermal wells was carried out from November, 1978 thru September, 1979. The program was comprised of three stages. In the first stage, the current state of knowledge on cementing of geothermal wells -- procedures and materials -- was defined through a search of open literature and personal interviews with knowledgeable individuals in the field.

The second stage was devoted to evaluation and screening of a number of cements and additives thought to be suitable for geothermal well cementing. In this stage, a large number of compositions were evaluated on the basis of their setting and thickening times.

In the third stage, cementing materials selected on the basis of second-stage findings were further evaluated in terms of their high-temperature setting behavior, strength development, cement-to-metal casing bond strength, permeabilities, and corrosive action on the steel well casing.

As a result of stage-three evaluations, several cementing compositions were successfully formulated which meet or exceed the requirements set by BNL RFP GP-1.

In the first-stage evaluations, a large number of cementing compositions were made up of various portland cements, oil well cements, and a number of additives and admixtures. Evaluations of approximately 1000 cementing compositions were made by curing at room temperature (25 ± 5)°C and in the autoclave at 205°C (401°F) and saturated steam pressure at that temperature (~ 1619 kPa). First, the cementing compositions containing

70 to 50% portland cements (Types I, III, and V) were mixed and cured in beverage cups with airtight lids at room temperature (25°C).

Viscosities of these slurries were measured at various time intervals until the limit of 100 P was reached. Those compositions with portland cements as the binders, which set within four to twenty-four hours at room temperature (25°C), were eliminated from further consideration. Those which did not set for seven days were further evaluated by autoclave curing at 205°C (401°F) and saturated steam pressure.

All the cementing materials formulated from the portland cements were eliminated as potential cementing materials for use in geothermal well completion as a result of first-stage evaluations. All compositions containing 40 to 70% portland cements (by weight of total solids) set in less than three hours in the autoclave at 205°C (401°F) and saturated steam pressure, and thus did not meet the thickening-time requirements set by the RFP GP-1. In addition, cementing compositions containing 40 to 60% oil well cements (Classes G, H and J), though not totally set, did not meet the thickening time requirements [viscosity not to exceed 100cP within three to four hours at 205°C (401°F) and saturated steam pressure].

The next stage in the study involved determination of thickening times, compressive strengths, and cement-to-metal bond strengths under autoclave conditions. Evaluations of the high-temperature thickening time were made at 205°C (401°F) and ~21,000 kPa (~3000 psi) pressure using the API high-temperature, high-pressure consistometer. Of forty cementing materials selected for evaluation, nine compositions were found to be worth further consideration for geothermal applications. On the basis of additional evaluation of the nine compositions, the five depicted in Table 1.1 have been submitted to the National Bureau of Standards (NBS) for continued evaluation.

Because of the thermal and pressure limitations in the testing equipment and the inordinate amounts of time necessary to carry out the measurements, the highest temperature and pressure used in the acquisition of the property data on cementing materials were 325°C (611°F) and 2100 kPa (300 psi), respectively. The apparent importance of testing strengths of geothermal

cementing material under in situ environments should not be underestimated. As can be seen in Table 1.1 the compressive strength is generally lower at elevated temperatures, but the relationship is not clear except to indicate the apparent inadequacy of room-temperature strength measurements.

Among the cementing materials suggested for use in geothermal applications, Class J oil well cement represents the component of highest cost. The only additional cost that may be incurred in the use of this composition would be the blending of various components, which is not considered prohibitive. The composition has been developed and designed to accommodate existing machinery and procedures used in current geothermal well-completion operations.

Table 1.1

Compressive Strength and Thickening Time of Cementing
Compositions Sent to NBS for Further Evaluation

Composition (wt%)	Compressive strength, kPa (psi) Cure time* and test temperature**								Thickening time, minutes, at 205°C
	1 Day		316°C	7 Day		28 Day		51 Day 205°C	
	25°C	205°C		25°C	205°C	25°C	205°C		
	25°C	205°C		25°C	205°C	25°C	205°C		
30-J/40-SF/30-P G	20,984 (3550)	17,888 (2600)	14,462 (2102)	24,080 (3500)	17,951 (2610)	13,148 (1910)	9,632 (1400)	9,632 (1400)	230
30-J/30-SF/40-BFS	11,834 (1720)	11,352 (1650)	12,739 (1847)	24,768 (3600)	19,608 (2850)	24,541 (3567)	8,944 (1300)	17,200 (2500)	160
30-J/30-P/40-BFS U	24,424 (3550)	9,976 (1450)	28,917 (4203)	26,144 (3800)	15,136 (2200)	25,855 (3758)	21,323 (3100)	26,822 (3900)	120
30-J/40-P/30-BFS F	18,920 (2750)	9,976 (1450)	14,917 (4203)	17,388 (2600)	15,136 (2200)	15,776 (2293)	13,072 (1900)	12,522 (1820)	340
30-J/35-SF/30-BFS/5-B	10,114 (1470)	8,944 (1300)	11,558 (1680)	19,264 (2800)	9,632 (1400)	10,370 (1580)	7,912 (1150)	11,008 (1600)	170

* Cured at 232°C (450°F) and saturated steam pressure.

** Tested 205°C (401°F) and saturated steam pressure 316°C
(600°F) and 2068 kPa (300 psi) steam pressure.

2. INTRODUCTION

The immediate objective of the program was to develop one or more cementing materials suitable for geothermal well completions which meet the minimum requirements set by BNL. These requirements were as follows:

- Placement ability, involving the capability of 3- to 4-hr retardation at expected placement temperatures.
- Compressive strength of more than 6895 kPa (1000 psi) 24 hr after placement.
- Bond strength-to-steel casing of more than 68.9 kPa (10 psi).
- Permeability to water of less than 0.1 millidarcy (md).
- Good mechanical stability and low permeability after prolonged exposure at high temperatures to brine solutions or dry steam.
- Noncorrosive to steel well casing.

The laboratory research effort in this program was comprised of four main work phases conducted from November, 1978 thru September, 1979.

- Phase I Define the current state of knowledge regarding cementing of geothermal wells -- procedures and materials.
- Phase II Select cements for 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.
- Phase IV Prepare a detailed final report of research procedures and findings and develop plans for further studies of potentially useful cementing compositions developed in the program.

In Phase II, criteria were established for the following:

1. Setting behavior of the cementing materials.
2. Strength behavior of the cementing materials.
3. Bond strength of the cementing materials to steel casing.
4. Permeability of the cementing materials.
5. Corrosion of the steel well casing by the cementing materials.
6. Characterization of the chosen cementing compositions.

3. EXPERIMENTAL

The total research program in the development of cementing materials for geothermal well completion was conceived as four main work phases.

3.1 Phase Definition of the Current State of Knowledge Regarding the Cementing of Geothermal Wells -- Procedures and Materials

The objective of this work phase was to identify, analyze, and document the experiences and research findings relating to the use of cementing materials for the completion of geothermal wells. The information and data of interest gathered from the open literature and through telephone and personal interviews with knowledgeable individuals from oil and cement companies. A summary of the literature review efforts in this program is presented in Appendix A.

3.2 Selection of Cements, Additives, and Admixtures for Laboratory Evaluation and Development and Use of Screening Procedures for Identifying the Most Promising Materials

3.2.1 Screening Procedures. On the basis of our understanding of the research problem and guided by the results of the first phase, we selected a number of cements, modifiers, and admixtures for evaluation. A list of

the materials selected is given in Table 3.1. A large number of cementing compositions -- hundreds of batches -- were formulated and screened on the basis of their rheological behavior, and thickening and setting times. If a given cementing composition could not be formulated (through the use of additives and admixtures) to meet the initial rheological requirements and long thickening times, it was not considered further regardless of its other properties.

The procedures followed for preparing the powdered batch and slurries and the measurements of viscosities were as follows. The powdered materials were weighed to the nearest tenth of a gram on a Mettler-Type P-1200 single-pan balance. One-kilogram powdered batches were mixed thoroughly in a double-cone blender. Powdered mixtures so prepared were put in a Waring blender, proper quantities of water already containing the assigned admixture were added, and the slurries were 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-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 higher water-solids ratios.

After mixing in the Waring blender, the slurries were poured into plastic cups and the initial viscosities of the slurries were measured with a Brookfield Model LVT viscometer having a number-3 circular disc spindle. After measurement of the initial viscosities, plastic cups containing cement slurries were tightly sealed with matching caps and set aside for curing at room temperature and pressure. Viscosities of the slurries were measured at various time intervals. A viscosity of 10,000 cP was the highest that could be measured with a No. 3 spindle on a Model LVT viscometer. The time at which the slurry reached this 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 the cementing industry.

3.2.2 Screening Results. A preliminary evaluation was made to determine the thickening time of over 1000 cementitious materials combinations at room

Table 3.1

List of Materials Considered in the
Development of Geothermal Cements

Material	Description	Supplier
<u>Cements</u>		
Oil well	Class G	Southwestern Portland, Victorville, CA
Oil well	Class H	Universal Atlas, Pittsburg PA
Oil well	Class J	" " "
Portland	Type I	" " "
Portland	Type II	" " "
Portland	Type V	" " "
Calcium aluminate	Lumnite	U. S. Steel
<u>Additives</u>		
Perlite	-325 Industrial #1 Ryolex	Silbrico Corp., Hodgkins, IL
Silica flour	Ottowa Grade 200	New England Silica Inc., South Windsor, CT
Slag	Granulated blast furnace	Edward Levy Co., Dearborn, MI
Bentonite	-200 Western	American Colloid
Pozzolan	Natural (ASTM C-618)	Airox-Earth Resources, Santa Maria, CA
Lime	Hydrate	Hamilton-Baker, Columbus, Ohio
<u>Admixtures</u>		
Carboxy methyl cellulose	Lot 55C-0069	Sigma Chemical Co., St. Louis, MO
Sodium hexameta phosphate	Lot 702408	J. T. Baker Chemical
Carboxy methyl hydroxy-ethyl cellulose	Lot 42-10	Polysciences Inc., Warrington PA

temperature $[(25 \pm 3)^{\circ}\text{C}]$; it should be noted that throughout this report 25°C is used for convenience in referring to room temperature]. The philosophy of the evaluation procedure was that the properties of the unset cement (initial viscosity and thickening time) would be subjected to the initial screening, followed by the physical properties of the hydrated cement. For this reason the water-solids content was used to achieve an initial viscosity of 1000 ± 200 cP. It was obvious that some of the materials required excessive amounts of water to achieve this viscosity and would be unable to satisfy the physical property criteria. They were, however, carried forward until they were eliminated by actual test.

On the basis of the room temperature screening, the material compositions depicted in Table 3.2 were evaluated further. This evaluation of viscosity and thickening at 205°C confirmed the results of previous studies which showed that portland and blended cements will exhibit excessive viscosity increases and short setting times in hot well environments. Compositions containing oil well cements, as expected, exhibited thickening and setting times much more suitable for geothermal applications. On the basis of our evaluation, Class J oil well cement was found to be the most desirable base material.

The minimum rheological requirements are dictated by the limitations imposed by the pumping equipment and pumping operations. These require that the cement slurries retain their fluidity (<100 P consistency) for the duration of a typical cementing operation (2 to 4 hr). Since a cementing composition that does not meet the thickening-time requirement is unacceptable regardless of its performance in other evaluation tests (e.g., compressive strength, bond strength, etc.), thickening-time measurements were chosen as the first task in Phase III in order to eliminate unsuitable compositions from further investigation.

3.3 Phase III: Evaluation of Promising Cementing Compositions

In this phase of the research project, cementing compositions showing promise on the basis of the screening evaluation in Phase II were subjected

Table 3.2

Cementing Compositions Selected for Phase-3 Evaluations
on the Basis of Initial Screening Results

Sample Number	Cements			Composition, wt%					Admixture	
	G	H	J	P	SF	HL	BFS	PT	CMC	CMHEC
1	70	-	-	30	-	-	-	-	0.5	-
2	70	-	-	-	30	-	-	-	0.5	-
4	70	-	-	-	-	-	30	-	0.5	-
5	70	-	-	-	-	-	-	30	0.5	-
6	70	-	-	30	-	-	-	-	-	0.5
7	70	-	-	-	30	-	-	-	-	0.5
9	70	-	-	-	-	-	30	-	-	0.5
10	70	-	-	-	-	-	-	30	-	0.5
11	60	-	-	40	-	-	-	-	0.5	-
12	60	-	-	-	40	-	-	-	0.5	-
14	60	-	-	-	-	-	40	-	0.5	-
15	60	-	-	-	-	-	-	40	0.5	-
16	-	60	-	20	20	-	-	-	0.5	-
17	-	60	-	20	-	20	-	-	0.5	-
18	-	60	-	20	-	-	20	-	0.5	-
19	-	60	-	20	-	-	-	20	0.5	-
20	-	-	60	20	20	-	-	-	0.5	-
21	-	-	60	20	-	20	-	-	0.5	-
22	-	-	60	20	-	-	20	-	0.5	-
23	-	-	60	20	-	-	-	20	0.5	-
24	-	-	40	30	30	-	-	-	0.5	-
25	-	-	40	30	-	30	-	-	0.5	-
26	-	-	40	30	-	-	30	-	0.5	-
27	-	-	40	30	-	-	-	30	0.5	-
28	-	-	30	70	-	-	-	-	0.5	-
29	-	-	30	-	70	-	-	-	0.5	-
31	-	-	30	40	30	-	-	-	0.5	-
32	-	-	30	40	-	30	-	-	0.5	-
33	-	-	30	40	-	-	30	-	0.5	-
34	-	-	30	30	40	-	-	-	0.5	-
35	-	-	30	30	-	40	-	-	0.5	-
36	-	-	30	30	-	-	40	-	0.5	-
37	-	-	30	60	10	-	-	-	0.5	-
38	-	-	30	60	-	10	-	-	0.5	-
39	-	-	30	-	10	60	-	-	0.5	-
40	-	-	30	10	60	-	-	-	0.5	-

to a more rigorous performance evaluation relating to their use in the lining of geothermal wells. Specifically, the effects of exposure to the downhole geothermal well environment on the properties and behavior of interest were examined.

3.3.1 Setting Behavior of the Cementing Materials. Thickening-time measurements on the cementing compositions meeting the Phase II performance criteria were the first studies to be made in Phase III. In these studies, cementing compositions that would meet minimum requirements set by BNL/DOE were identified. The thickening-time experiments were carried out using the high-temperature, high-pressure consistometer described in Appendix B. These tests were carried out at Dowell Laboratories, Tulsa, Oklahoma.

Thickening-time determinations were made on cementing compositions containing 30 to 60% oil well cements. Thickening-time values on selected compositions containing 30% Class J oil well cement ranged from 2 to >5 hr, with an average value >3 hr for nine samples (Table 3.3). The reported thickening times on the cementing compositions were obtained using 0.5% carboxy methyl cellulose (CMC) as a retarding admixture. Thickening times of sample No. 3 (30% pozzolan and 40% blast furnace slags) were also measured using Dowell's D-100 admixture (a proprietary admixture developed by Dowell Division of Dow Chemical Company) with amounts of 6 to 7.5%. Thickening times determined using this admixture showed a 20 and 50% increase over 0.5% CMC samples, for 6 and 7.5% D-100, respectively. Admixture D-100 seems appropriate in controlling the thickening times of these compositions. According to Dowell chemists, relatively large quantities of the D-100 admixture can be used as required to increase the thickening times.

As the numbers in Table 3.3 indicate, the thickening times exhibit a wide range of values. The mechanistic effects of various additives (silica flour, pozzolan, and blast furnace slags) are not well understood at this stage; but it appears that, for example, blast furnace slags seem to lower the thickening times compared with the effects of silica flour and pozzolan, which appear to increase the thickening times of the

Table 3.3
Setting Behavior of Various Cementing Compositions
Based on Class J Cement at 204°C (400°F)

Sample No.	Composition, wt%	W/C	Thickening time, min
1	30-J/40-SF/30-P	0.5	230
2	30-J/40-SF/30-BFS	0.5	160
3	30-J/30-P/40-BFS	0.5	120, 145*, 180**
4	30-J/40-P/30-BFS	0.5	340
5	30-J/35-SF/30-BFS/5-B	0.5	170
6	30-J/70-BFS	0.5	120
7	30-J/70-P	0.5	120
8	30-J/60-BFS/10-SF	0.5	140
9	30-J/60-P/10-SF	0.5	300

* 6% D-100.

** 7.5% D-100.

cementing slurries. This, however, is only an empirical observation. The effects of one component; in turn, seem to vary depending on the nature and amounts of other additives. Blast furnace slag and pozzolan combinations, for example, yield shorter thickening times than blast furnace and silica flour combinations.

On the basis of limited efforts, carboxy methyl cellulose was found to be the most effective retarder (single chemical) in this project. Unfortunately, elaborate efforts to develop set retarders for geothermal cements were beyond the scope of the present study. Such a study, leading to the development of retarding admixtures to be used in various geothermal environments, would be very useful to the overall geothermal energy development program.

Figure 3.1 is an example of the thickening-time data obtained on cement slurries. The figure depicts the viscosity (consistency) and temperature profiles for the given composition. The temperature profiles indicate the heating rate of the slurries during the experiment. A very significant feature of the viscosity versus time curves is that viscosities remain relatively constant with time as a function of temperature rise rather than gradually increasing. This is a very desirable feature of the slurries. An ideal cement slurry in geothermal well completion operations should exhibit low (≈ 50 cP) and constant viscosity throughout the cementing operation and set shortly after the cementing of the well is completed. The observed viscosity behavior of the cementing compositions indicates that these compositions exhibit this property, that is, low and constant viscosity over a long time followed by a sudden rise. In Figure 3.1, for example, the cement slurry retains its original viscosity up to about 20 minutes, then rises to about 50 cP (which is still quite pumpable) and remains at that value up to 220 minutes before rising to a value above 100 cP. Constant viscosity is also desirable in preventing possible disruptions in pumping operations that may result from variations in viscosities. The pumping rates can be influenced by variable slurry viscosities which may result in uneven pumping and even more serious interruptions such as equipment breakdown.

Figure 3.1. Temperature and viscosity profiles from the API high-temperature consistometer.

3.3.2 Evaluation of Strength Behavior. The compressive strengths of systems showing the greatest potential were measured as a function of time and specimen temperature. The following procedure was used to prepare the specimens:

1. Cast specimens in cylindrical molds (2.54 cm diam by 1.5 cm length) at room temperature and ambient pressure.
2. Immediately place molds in autoclave and cure hydrothermally for 24 hr at 232°C (450°F) and saturated steam pressure. Autoclave is heated at 1°C/min.
3. Cool autoclave (10°C/hr) and remove and demold all specimens. Return specimens for later test to autoclave and reheat to 232°C (450°F) and saturated steam pressure.
4. Prepare 2.54 cm-long specimens and determine their room temperature compressive strength.
5. Determine the hot compressive strength (205°C) using the hot-can apparatus described in Appendix B. Specimens are heated at 2°C/min to 205°C and held at that temperature for 1 hr prior to testing.
6. Repeat steps 3 to 5 after 7, 28, and 51 days of autoclave curing.

Table 3.4 depicts the compressive strength results of specimens cured and tested by this procedure. As can be seen, all of these compositions exhibit compressive strengths in excess of the 700 kPa (1000 psi) target. The main contribution of these data, however, is confirmation of the importance of testing physical properties under conditions representative of the geothermal use environment. The materials tested at 205°C consistently displayed lower strengths than those tested at 25°C. This is a clear indication that the use of room temperature test data to design a cementing system may result in unacceptable performance. Specimens tested at 316°C (2100 kPa/305 psi steam pressure as opposed to saturated steam pressure for the 205°C testing) actually showed strength increases in most cases. However, since they had only been autoclave cured for one day at

Table 3.4
Compressive Strength of Class J Cement Compositions
Cured at 232°C (450°F) and Saturated Steam Pressure

Compressive strength, kPa (psi)										
Sample No.	W/C	Composition, wt%	Autoclave cure time, Days							
			1		7		28		51	1
			Specimen test temperature†, °C		Specimen test temperature†, °C		Specimen test temperature†, °C		Specimen test temperature†, °C	Specimen test temperature†, °C
			25°	205°	25°	205°	25°	205°	25°	316°
1	0.5	30-J/40-SF/30-P	20,984 (3005)	17,888 (2600)	24,080 (3500)	17,951 (2610)	13,148 (1910)	9,632 (1400)	9,632 (1400)	14,462 (2102)
2	0.5	30-J/30-SF/40-BFS	11,834 (1720)	11,352 (1650)	24,768 (3600)	19,608 (2850)	24,541 (3567)	8,944 (1300)	17,200 (2500)	12,739 (1847)
3	0.5	30-J/30-P/40-BFS	24,424 (3550)	9,976 (1450)	26,144 (3800)	15,136 (2200)	25,855 (3758)	21,328 (3100)	26,822 (3900)	28,917 (4203)
4	0.5	30-J/40-P/30-BFS	18,920 (2750)	12,284 (1800)	17,888 (2600)	15,136 (2200)	15,776 (2293)	13,072 (1900)	12,522 (1820)	14,895 (2165)
5	0.5	30-J/35-SF/30-BFS/5-B	10,114 (1470)	8,944 (1300)	19,264 (2800)	9,632 (1400)	10,870 (1580)	7,912 (1150)	11,008 (1600)	11,558 (1680)
6	0.5	30-J/70-BFS	14,104 (2050)	13,072 (1900)	12,384 (1800)	8,944 (1300)	8,765 (1274)	7,224 (1050)	23,392 (3400)	17,706 (1120)
7	0.5	30-J/70-P	14,998 (2180)	8,156 (1200)	15,858 (2300)	11,136 (2200)	11,042 (1605)	10,320 (1500)	11,456 (1660)	16,478 (2345)
8	0.5	30-J/60-BFS/10-SF	14,104 (2050)	14,448 (2100)	15,824 (2850)	9,632 (1400)	16,650 (2420)	12,384 (1800)	11,421 (2140)	13,598 (1976)
9	0.5	30-J/60-P/10-SF	14,104 (2050)	11,008 (1600)	22,016 (3200)	17,200 (2500)	12,618 (1834)	9,632 (1400)	11,008 (1600)	16,911 (2458)

† 205°C test was with saturated steam pressure, 316°C was with 300-psi steam pressure.

a lower temperature, the changes in strength may be a combination of increased reaction and lower steam pressures. There could be some question as to whether the 10°C/min autoclave cooling and 2°C/min reheat rate constitute a thermal shock to the specimen. At present, these rates are not believed to be too rapid. However, it may be wise to develop a procedure to test those materials which does not require a cooling and reheating step.

The strength data obtained on the cementing compositions at both room temperature (25°C) and elevated temperatures (205°C and 325°C) have also helped to explain the contribution of different components to the compressive strength of cementing materials. For example, cementing compositions with blast furnace slag additions show higher strength than compositions without such additions. Furthermore, high-temperature mechanical stability of these compositions is also significantly improved as evidenced by the compressive strength values after 51 days of curing.

3.3.3 Cement-to-Metal Bond Strength Measurements. Cement-to-metal bond strength measurements were carried out both at room temperature and in the hot-can assembly using 2.54 cm diameter specimens cast around 0.635 cm steel rods, as described in Appendix B. The cement-to-metal bond strength is described as the force required to push the metal rod through the cast cements with unit area of interface between the metal and cement.

Measurement of the shear force to separate the steel rod from the cement was chosen over the actual tensile bond strength of the metal-cement interface for practical reasons. Because of the very low bond strength after 24 hours of hydration, the tensile methods would not provide accurate and meaningful bond strength data.

Cement-to-metal bond strength data obtained on the nine compositions are shown in Table 3.5. All the cementing compositions tested for cement-to-metal bond strength requirements showed more than adequate strength, including the compositions presented in Table 3.5. Bond strength measurements were made both at room temperature and at 205°C (saturated steam pressure). It is obvious from the data that bond strength values at 205°C are even higher than the room temperature values. Thermal expansion

Table 3.5

Cement-to-Metal Bond Strength of Compositions with 30% Class J
Oil Well Cement Cured at 232°C (450°F) for 1 Day

Cement Composition	Amounts	Admixture	W/S	Bond strength, kPa (psi) 25°C	Bond strength, kPa (psi) 205°C
SF	40	CMC	0.5	3519 (510)	4658 (675)
P	30				
SF	30	CMC	0.5	2845 (407)	3298 (478)
BFS	40				
P	30	CMC	0.5	2332 (338)	3567 (510)
BFS	40				
P	40	CMHEC	0.5	4568 (662)	1932 (280)
BFS	30				
SFB	35	CMC	0.5	2022 (293)	2415 (350)
BFS	30				
B	5				
BFS	70	CMC	0.5	1949 (210)	3692 (535)
P	70	CMC	0.5	1601 (232)	2503 (363)
BFS	60	CMC	0.5	3077 (446)	2505 (694)
SF	10				
P	60	CMC	0.5	3340 (484)	3692 (535)
SF	10				

differences between the steel bar and the cement is believed to be the reason for the observed higher bond strength values at high temperatures.

3.3.4 Cement Permeabilities. Permeability measurements were made on a large number of cements as described in Appendix B. Both water and helium permeabilities were measured. Almost all the cements showed permeabilities of 0.1 md or lower, thus meeting the requirements imposed on them as candidates for use in the completion of geothermal wells.

Helium permeabilities were made at 1 atmosphere pressure gradient across the cement sample, whereas the pressure gradient was 100 atm for the water permeability measurements, thus, complying with the standard API test for permeability of oil well cements.

The results of permeability tests on the final nine cementing compositions are listed in Table 3.6. A careful look at the table indicates that silica flour and pozzolan improve the permeability of the cementing compositions, whereas the blast furnace slags have detrimental effects on permeabilities. Visual and microscopic examinations of the permeability specimens support the results of the experiments.

3.3.5 Corrosion Behavior of the Steel Well Casing by the Cementing Materials. The electrochemical nature of the corrosion process for steel in concrete has allowed development of nondestructive techniques for following the progression of steel corrosion. The great advantage of such techniques is that the onset and progress of the corrosive action of the cementing medium on steel can be determined before visual and structural manifestations, such as delamination, cracking, and spalling due to stress development by expanding corrosion products.

Previous studies¹⁻³ have demonstrated that the half-cell potential of steel in concrete is a valid indicator of corrosion activity. The corrosion of steel in concrete probably results from current flow between both macroscopically and microscopically separated anodes and cathodes. The anodes and cathodes can occur on the same steel reinforcing member (or steel casing in geothermal wells) or on widely separated steel members. In a geothermal well the part of the steel casing which is more exposed to

Table 3.6

Water and Helium Permeabilities of Selected Cementing Compositions With 30% Class J Cement After 1-Day's Curing at 232°C (450°F) and Saturated Steam Pressure

Cementing composition	Amounts	Admixture	W/C	Helium permeability,* md	Water permeability,** md
SF	40	CMC	0.5	2.1×10^{-4}	6.2×10^{-3}
P	30				
SF	30	CMC	0.5	4.3×10^{-3}	5.1×10^{-2}
BFS	40				
P	30	CMC	0.5	3×10^{-3}	3×10^{-2}
BFS	40				
P	40	CMHEC	0.5	6×10^{-3}	2×10^{-2}
BFS	30				
SF	35	CMC	0.5	8×10^{-3}	3.3×10^{-2}
BFS	30				
B	5				
BFS	70	CMC	0.5	6×10^{-2}	2.1×10^{-1}
P	70	CMC	0.5	4.2×10^{-3}	2×10^{-2}
BFS	60	CMC	0.5	3.5×10^{-2}	1×10^{-1}
SF	10				
P	60	CMC	0.5	7.4×10^{-3}	3.2×10^{-2}
SF	10				

* 1 atmosphere pressure gradient.

** 100 atmosphere pressure gradient.

a thermochemical environment (brine or flashing brine) would frequently act as an anode and the end that is relatively isolated would act as a large cathode.

Corrosion data on five different cementing compositions are summarized in Figure 3.2. The band between -0.28 and -0.32 V is considered to be a demarcation line between the corroding and noncorroding conditions. Half-cell potential values less than -0.28 V indicate the absence of any appreciable corrosion, whereas values below -0.32 V (numerically greater) are an indication of significant corrosion.

Among the half-cell potential data on five cementing compositions in Figure 3.2, all but one show lower values -- increased resistance to corrosion -- with curing time. The potential values for these compositions are well above the critical value (-0.32 to -0.28 V) at 21 days' curing. The behavior of sample No. 4 (high point of -0.45 V) at this time is not understood. Repeated measurements on the sample produced the same result.

Potential measurement methods are not without their problems, however, as the sole arbitrator of corrosion. The method, by its very nature, is a qualitative measurement which cannot be precisely related to a corrosion rate. The corrosion rate is the parameter which may need to be determined in geothermal wells. Nevertheless, the results of the laboratory work indicate that a nondestructive means for measuring or detecting corrosion activity of steel can be useful in evaluating cement and concrete structures exposed to aggressive environments. However, whenever the half-cell potential values are interpreted in terms of steel corrosion activity it is important to recognize that:

1. the half-cell potential of steel can only be empirically related on a statistical basis to cement failure under specific conditions;
2. the half-cell potential does not measure the physical condition of the cement medium; and
3. any possible structural damage to the cement due to corrosion of the steel casing is related to cement strength, absorption, moisture

content, other chemical species, stresses, and its thickness around the steel casing.

Figure 3.2. Half-cell potentials of steel in various cementing compositions. (Numbers 1 through 5 correspond to compositions in Table 1.4.)

In view of the fact that the steel casing in geothermal wells is exposed to cement on one side and an aggressive geothermal environment on the other, the failure rate (or the life) of the casing will depend on the severity of the geothermal medium (brine, flashing brine, and steam) rather than the corrosion due to the cementing medium. The corrosive action of the cement on the steel casing would be minimal by comparison with the effects of the geothermal environment.

3.3.6 Characterization of Cementing Materials. An attempt was made to correlate the chemical and morphological characteristics of the cement compositions with their respective physical properties and performance. The methods of characterization used were DTA/TGA, XRD, and scanning

transmission electron microscopy (STEM) coupled with energy dispersive x-ray analysis (EDS). This correlation attempt was unsuccessful due to an inability to reliably perform the characterization work.

The principle problems were associated with the critical impact of differing and unknown crystallinity differences and the requirement to analyze a large number of samples. The correlation of bulk properties such as strength and corrosion behavior is apparently possible only after the establishment of a large characterization data base. The variability of characterization data obtained in this program was extreme and unreliable.

The only useful interpretation of the work was that tobermorite is the major hydration product. This is in agreement with the work and conclusions of Kalousek¹ at the Colorado School of Mines. The mechanism of hydration in these systems and the factors which could be used to enhance tobermorite formation could not be identified. A detailed and extensive characterization effort will be required to overcome the microstructural and chemical inhomogenities if an understanding of the reaction mechanisms is to be developed.

4. CONCLUSIONS

As concluding remarks, the following summary of this program can be given:

1. Several cementing compositions withstanding a simulated geothermal condition (autoclaving at 232°C and at saturated steam pressure through 51 days) have been developed.
2. The problem of steel-casing corrosion due to the cementing materials seems negligible in view of the corrosion caused by the geothermal fluids.
3. All cementing materials seem to develop good bond strength with the steel well casing.
4. Mechanical strength and permeability of all the cementing materials found to be suitable, improve after up to 51 days' exposure to high-temperature, high-pressure steam.
5. Meeting the thickening-time requirements proved to be the most difficult task in the research project. Several practical problems were encountered in the thickening-time measurements at Dowell, e.g., sticking of the cement slurry to the stirring pedal, which led to erroneous measurements or unexplained behavior in the thickening-time curves. A method which more effectively simulates the pumping procedures may have to be developed for these measurements.
6. Among the additives used in the development of the cementing compositions, silica flour and pozzolan increase the thickening times and improve the permeability of cements, but strength development is retarded.
7. Addition of blast furnace slag as an additive appears to significantly improve the strength development and high-temperature stability. This is believed to be

due to the formation of quantities of tobermorite in the presence of blast furnace slag. Compositions with blast furnace slags, however, exhibit lower thickening times and somewhat higher permeabilities. Higher permeabilities may be due to higher porosities in thin samples, perhaps resulting from evolution of sulfur gases during the hydrothermal curing of the samples. H_2S evolution was noticed during mixing of some cementing compositions containing blast furnace slags.

8. A series of satisfactory cementing compositions can be formulated from Class J oil well cement, pozzolan, silica flour, and blast furnace slags, some of which were developed in this study.
9. A-Tobermorite appears to be the major hydration product accounting for the strength development in the compositions formulated. Reactions and conditions leading to A-tobermorite formations in compositions containing blast furnace slags should be further studied.
10. The long-term stability of the cementing compositions remains unconfirmed.

It is hoped that after the pilot plant evaluations of the five cementing compositions submitted to NBS (see Tables 1.4 and 3.4), the recommended cementing materials will be subjected to field tests to further demonstrate their suitability for geothermal well completion.

Although some of the anticipated test data could not be acquired (e.g., strength and thickening-time data at $415^{\circ}C$ ($780^{\circ}F$) because of unforeseen instrumental and/or cost limitations, the cementing compositions suggested for further evaluations (compositions 1 to 5, Table 3.4) still hold great promise for use in geothermal applications. The fact that compressive strengths do not show a significant decline at test temperatures as high as $325^{\circ}C$ ($620^{\circ}F$) is an indication that higher temperature durability of these compositions can be expected. This should be investigated further, using samples which are cured at higher temperatures and steam pressures.

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APPENDIX A

LITERATURE SURVEY

Cementing Operations

An excellent account of 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: (1) to enable effective stimulation treatments, (2) to aid proper reservoir evaluation, (3) to prevent annular communications with unwanted fluids, (4) to prevent lifting of excessive well fluids, and (5) to 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 A-1.

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

- Care should be taken to select the proper cementing material that suits the well requirements.
- Bulk handling and storage facilities are very important both economically and technically.
- "Essential volume" of water supply is necessary 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 ensure the correct water/solids ratio.

Table A-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 or 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

- 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 a 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.
- Flotation factor in big pipes should be considered.
- Flotation of large-diameter pipes can become a problem during cementing. To deal with this, the pipe is unchained 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-storing cementing through drill pipe.
- (4) Outside cementing through tubing.
- (5) Reverse circulation cementing.
- (6) Delayed set cementing.
- (7) Multiple string cementing.

Figure A-1. Methods of placing cement downhole.

Detailed descriptions of the above techniques can be found in refs. 4 through 9 at the end of this report. Fig. A-1 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 moving casing before cementing.
- (5) Heavier mud systems.
- (6) Increasing difficulty 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. It is used to obtain a seal between the casing and the formation to isolate the downhole water. The technical literature contains a wealth of information on squeeze cementing,^{12,13} but many unconsidered questions remain:

- Where does the cement go on a squeeze job?
- What is formation breakdown? Is it necessary?
- Should water or mud be used for breakdown?
- Can perforations be plugged with cement?
- Can the quantity of cement be controlled during cementing?

With improved understanding of rock fracture mechanics and filtration properties of cement slurries, the number of squeeze cementing applications have been increased significantly. Squeeze cementing is used in the following operations⁴⁻⁶:

- 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.

In addition to 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 applications are beyond the scope of this report. Interested readers can refer to the references listed at the end of this Appendix for further information.¹²⁻¹⁷

Smith¹ 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 the slurry becomes sufficiently high to prevent its pumping. Related to well depth are temperature and pressure, which affect how long the slurry will pump and how well it develops the strength necessary to support pipe. Temperature has the more pronounced influence.¹⁸

The density of a cement slurry should always be great enough to maintain well control. The density of slurries can be controlled either by regulating 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 articles¹⁹⁻²² 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 exposed to the severe thermal, chemical, and pressure conditions of such wells. The lack of research in geothermal cements is certainly due to the fact that geothermal resources were not considered as alternative energy supplies until the recent worldwide energy crisis.

The proceedings of the United Nations Symposium on Geothermal Resources in Pisa, Italy (1970), is probably the most substantial single scientific document on the subject. Even in this symposium the cementing problems, chemical compositions, and thermal characteristics of various geothermal sites were studied in conjunction with methods of extracting minerals from geothermal brines.²⁴ Table A-2 depicts elemental and mineral contents of several geothermal wells around the world. As Table A-2 indicates, these minerals may cause several problems in a geothermal installation: 1) corrosion, 2) deposition, and 3) erosion. Of the ions present, Cl^- is the most corrosive. Problems may also be encountered with dissolved gases, e.g., CO_2 , H_2S , etc. Corrosive action of these gases is 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 the need for improved cementing materials has been mentioned.¹⁹⁻²¹ Matsuo²¹ briefly discusses casing and cementing problems encountered in drilling for geothermal steam, specifically mentions the difficulty of placing the cement slurry in the well, and emphasizes the importance of

Table A-2

Some Geothermal and Nongeothermal Brine Analyses, In ppm of Dissolved Ions

Constituent	Geothermal			Nongeothermal		
	Niland, Imperial Valley, Calif. IID No.	Cerro Prieto, Mexico Well M-8	Wairakei, New Zealand	Ocean	Oilfield High salinity	Brines 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, °C	340	-	-	-	-	-
Total	258,973	21,915	4,237.5 to 4,239.0	34,486	335,865	15,417

rheological characteristics of fresh cement slurries. Most cement failures are attributed to high temperatures²⁰ 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, making it essential to ensure the compatibility of cement slurries with the drilling mud.

Typical cementing compositions used in cementing geothermal wells²³⁻²⁵ have been low-aluminate portland cements containing 20 to 50% silica flour as additives along with retarders, friction reducers, and anti-foaming 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, and phosphate slags have been tried as plugging cements^{25,26} in numerous geothermal well sites.

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APPENDIX B

EXPERIMENTAL TECHNIQUES AND EQUIPMENT

High-Temperature, High-Pressure Setting Behavior -
Thickening-Time Tests

Thickening-time tests are designed to determine the length of time a given cement slurry will remain sufficiently fluid as to be pumpable with the available equipment. Thus, the thickening-time measurements serve as a method of comparing cementing compositions.

A pressurized high-temperature consistometer developed by Amoco Production Company* was used in the thickening-time measurements.

Briefly, the procedure was to prepare the slurry to be tested, place it in the thickening-time tester (high-temperature, high-pressure consistometer), apply pressure and increase temperature until desired conditions are reached, and record the consistency as a function of time. Complete details of the procedure with various schedules are given in API code RP 10B titled "Recommended Practice for Testing Oil Well Cements."

The high-pressure - thickening-time tester, depicted in Figure B-1, consists of a rotating cylindrical slurry container equipped with a stationary-paddle assembly, all enclosed in a pressure chamber designed for a working pressure of 3625 kPa (25,000 psi) at a maximum temperature of 205°C (401°F). Pressure is generated by an air-operated hydraulic pump and a complete hydraulic system with the normal reservoir, piping, valves, filters, and other required items. Heat is supplied by a 3,000-W, internal-tubular heater controlled by a variable transformer and Pyrometer Controller. Thermocouples are provided for determining the temperature of the oil bath and of the cement slurry. The slurry container is rotated at a constant speed of 150 rpm by a motor and appropriate gear reduction. The consistency of the cement slurry is indicated and recorded as a dc voltage obtained from a potentiometer mechanism within the pressure cylinder, which contains a standardized torsion spring to resist the rotating tendency of the paddle.

* Further information pertaining to the consistometer may be obtained from Chandler Engineering Company, 7707 E. 38th Street, Tulsa, Oklahoma 74145.

Figure B-1. Typical pressurized consistometer.

This rotational tendency is proportional to the consistency of the cement slurry. Valves, switches, pilot lights, and other accessories are provided to make a completely integrated instrument. It is enclosed in a stainless steel cabinet with overall dimensions 152.4 cm (60 in.) high x 83.8 cm (33 in.) wide x 73.7 cm (29 in.) deep.

Since there was no API schedule describing the thermal and pressure conditions of interest to this program such as may be encountered in geothermal wells, a modified version of schedule 32 was employed in the project. Table B-1 is schedule 32 as described by API code RP 10B. The heating rate of the cementing composition in the high-temperature, high-pressure consistometer was about 7.5°C/min. The final thermal and pressure condition was usually attained in 45 to 50 minutes, and was then held constant for the duration of the experiment.

Measurement of Compressive Strength

In a program for the U. S. Atomic Energy Commission, completed at Battelle in 1969, a technique was developed for measuring the strength and elastic properties of portland cement concrete at temperatures up to 150°C* under saturated steam pressures. These measurements were carried out in a specially designed pressure-can assembly shown in Figure B-2. The pressure can was constructed from 0.95 cm (3/8-in.)-thick stainless steel and has a removable lid for access to the specimen chamber. In the figure, a 10.2 x 20.3 cm (4 x 8-in.) concrete cylinder is represented as the test specimen, although other specimen geometries can be used. A stainless-steel bellows assembly in the lid permits the transfer of a uniaxial compressive load to the specimen, while the specimen is at temperature under saturated steam pressure.

A large Nichrome split-shell furnace (not shown in Figure B-2) was used around the body of the pressure can to gain the desired temperature in the specimen. Heat losses from the ends of the can were minimized by the use of cartridge heaters in the bottom and insulation at the top of the can.

* This high-temperature pressure cell was later modified to enable us to obtain limited compressive strength data at 325°C and 21,000 kPa pressure.

Table B-1
6100-m (20,000-ft) Casing-Cementing
Well-Simulation Test-Schedule 32 (partial)

Time, min	Pressure, psi kg/cm ²	Temperature Gradient, °F/100 ft depth			
		1.1		1.5	
		°F	°C	°F	°C
0	2000 (140)	80 (27)		80 (27)	
2	2900 (204)	88 (31)		92 (33)	
4	3800 (268)	96 (36)		104 (40)	
6	4700 (332)	104 (40)		117 (47)	
8	5600 (396)	113 (45)		129 (54)	
10	6500 (460)	121 (49)		141 (61)	
12	7500 (524)	129 (54)		153 (67)	
14	8400 (588)	137 (58)		165 (74)	
16	9300 (651)	145 (63)		177 (81)	
18	10200 (715)	153 (67)		190 (86)	
20	11100 (779)	161 (72)		202 (94)	
22	12000 (843)	169 (76)		214 (101)	
24	12900 (907)	178 (81)		226 (108)	
26	13800 (971)	186 (86)		238 (114)	
28	14700 (1035)	194 (90)		251 (122)	
30	15600 (1099)	202 (94)		263 (126)	
32	16500 (1163)	210 (99)		275 (135)	
34	17500 (1227)	218 (103)		287 (142)	
36	18400 (1291)	226 (108)		299 (143)	
38	19300 (1355)	235 (113)		311 (155)	
40	20200 (1419)	243 (117)		324 (162)	
42	21100 (1482)	251 (122)		336 (169)	
44	22000 (1546)	259 (126)		348 (176)	
Heating Rate, °F/min		4.07		6.09	
°C/min		2.25		3.39	
Static bottom-hole temp		300(149)		380(194)	

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

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

From 5-75, Cem.

Sec. II-C sup. 1RP 10B

The can is fitted with pressure-tight thermocouple glands, a pressure gauge, a pressure-relief valve, and a safety-blowout disc.

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

Figure B-2. Schematic of the pressure-can test assembly used in measuring the compressive strength of concrete at elevated temperatures under saturated steam pressure (shown with 10.2 x 20.3 cm [4 x 8 in.] concrete cylinder specimen).

Measurements of Permeability

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

Liquid and gas permeabilities were measured at room temperature using water and helium as the permeating media and employing the apparatus shown in Figure B-3 (a slightly modified version of this apparatus was used for liquid permeability measurements). Specimens, 2.54 cm (1 in.) in diameter and 0.63 cm (1/4 in.) thick, were used as permeability samples. The cylindrical-disc cement specimen was inserted in the specimen holders (A) and (B). A rubber gasket and a latex sealing material provided the seal between two ends of the specimen. The amount of fluid permeating through the material in a given time was measured. Permeability values were calculated from the experimental data employing Darcy's law.

According to Darcy's law:

$$K = 14,700 \frac{QL}{AP} ,$$

where

- K = Permeability in md (mol)
- Q = Fluid flow rate in ml/sec
- μ = Fluid viscosity in cP
- L = Sample length in cm
- A = Sample cross-sectional area in cm²
- P = Differential pressure in psi

Figure B-3. Schematic drawing of the permeability apparatus.

Investigation of the Bond Strength Between the Cementing Material and the Steel Casing

This work was conducted using specially prepared specimens as shown in Figure B-4. The specimens were prepared by inserting a 5.1 cm (2-in.)-long, 0.63 cm (1/4-in.)-diam. steel rod in a 5.1 cm (2-in.)-long, 2.5 cm (1-in.)-diam. cylindrical specimen mold prior to casting the cement. The rod was parallel to the long dimension and coaxial with the longitudinal axis of the specimen. The cement was cast to a depth of 3.8 cm (1-1/2 inches). The specimens were placed in the autoclave assembly and cured for a prescribed length of time at a predetermined pressure and temperature.

For the cement-to-steel bond strength measurements the specimens were placed in the pressure-can assembly set up on the Instron machine. The pressure can and specimen then were brought up to the desired test temperature (with saturated steam in the pressure can), and temperature equilibrium was established. At this point the force required to move the steel rod through the cement specimen was measured. The bond strength was calculated as the shear force necessary to move the steel rod through the cement divided by the interfacial surface area between the cement and the steel rod.

Measurement of Steel Casing Corrosion by Cements

Previous studies¹⁻³ have demonstrated that the half-cell potential of steel in concrete is a valid indicator of corrosion activity. The corrosion of steel in concrete probably results from current flow between macroscopically and microscopically separated anodes and cathodes. The anodes and cathodes can occur on the same steel reinforcing member (or steel casing in geothermal wells) or on widely separated steel members. In a geothermal well the part of the steel casing which is more exposed to a thermochemical environment (brine or flashing brine) would frequently act as an anode, and the end that is relatively isolated from such environment would act as a large cathode.

Figure B-4. Specimen configuration for investigation of bond strength between the cementing material and the steel casing.

Because of the macroscopic separation of anodes and cathodes, and the relatively high resistance of electrolyte (cement) path between them, the differing electrode potentials of the corroding (anodic) and noncorroding (cathodic) steel areas can be determined by using a reference electrode half-cell situated on the surface of the cement. By conducting a "scan" of the cement surface, the areas of active corrosion can be delineated. Potential measurement methods were utilized as the corrosion estimation technique in the present study.

There is confusion regarding the presentation of the potential values exhibited by the reinforcing bar in concrete (rebar). The potential of the rebar is almost always active (negative) to the Cu/CuSO_4 reference electrode, and thus should be reported as such (e.g., $-0.35 \text{ V}_{\text{CSE}}$). More active corrosion gives a more negative potential (e.g., $-0.50 \text{ V}_{\text{CSE}}$), whereas passive rebar gives a more positive (noble) potential (e.g., $-0.15 \text{ V}_{\text{CSE}}$). However, bridge maintenance engineers frequently disregard the sign of the potential, and

sometimes a numerically larger number signifies a more active potential. When the Cu/CuSO_4 is used as the reference cell, it has been established that the steel reinforcement may be considered to be actively corroding when the measured potential is more active (negative) than -0.35 V. If the measured voltage is more positive (noble) than -0.30 V, the steel is still in a passive state. Using this technique, it is possible to map a concrete surface to show contours of equipotentials and thus identify the active and passive areas of the steel in the deck (Figure B-4). The electrical potentials must be measured using a high input impedance voltmeter to overcome the high resistance of the concrete electrolyte. A schematic of the setup is shown in Figure B-5.

The technique is currently being considered for adoption as a standard test by ASTM. With respect to the interpretation of results, this standard currently reads:

- (1) If potentials over an area are numerically less than -0.20 V CSE, there is a greater than 90% probability that no reinforcing steel corrosion is occurring in that area at the time of measurement.
- (2) If potentials over an area are in the range of -0.20 to -0.35 CSE, corrosion activity of the reinforcing steel in that area is uncertain.
- (3) If potentials over an area are numerically greater than -0.35 V CSE, there is a greater than 90% probability that reinforcing steel corrosion is occurring in that area at the time of measurement.

Although the half-cell potential is a valid indicator of corrosion activity of steel in concrete, it does not correlate directly with the corrosion rate. However, qualitatively, with an increasing amount of corrosion, the numerical value of the potential also increases.

Figure B-5. Copper-copper sulfate half-cell circuitry.
(From proposed ASTM standard on half-cell potentials of reinforcing steel in concrete.)

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