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**DEVELOPMENT OF GEOTHERMAL WELL
COMPLETION SYSTEMS**

Final Report

**By
Erik B. Nelson**

Work Performed Under Contract No. AC02-77ET28324

**Dowell Division
Dow Chemical U.S.A.
Tulsa, Oklahoma**

**U. S. DEPARTMENT OF ENERGY
Geothermal Energy**

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DEVELOPMENT OF GEOTHERMAL WELL COMPLETION SYSTEMS
FINAL REPORT

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ABSTRACT

Results of a three year study concerning the completion of geothermal wells, specifically cementing, are reported. The Department of Energy (DOE) funded research involved some specific tasks: (1) determination of properties an adequate geothermal well cement must possess; (2) thorough evaluation of current high temperature oilwell cementing technology in a geothermal context; (3) basic research concerning the chemical and physical behavior of cements in a geothermal environment; (4) recommendation of specific cement systems suitable for use in a geothermal well.

EXECUTIVE SUMMARY

This report documents the results of a three year study, funded by the Department of Energy (DOE), to develop cement systems suitable for the completion of geothermal wells. Geothermal wells are completed in much the same manner as conventional oil wells; however, the environment with which completion materials must contend in a geothermal environment can be much more severe. For example, the bottom hole temperature in a geothermal well can be as high as 370°C (700 F), and the formation brines downhole are often extremely saline and corrosive. Failure of a geothermal well due to inadequate cementing materials could result in severe economic and environmental consequences. Thus, current high temperature oil well cementing technology, as well as some unconventional cementitious systems, was thoroughly evaluated with the goal of identifying suitable materials that would perform satisfactorily in such a critical environment.

To better define the geothermal problem and determine the properties a geothermal well cement must possess, several operators and engineers with geothermal expertise were interviewed. The interviews cleared up several misconceptions concerning geothermal well completions; notably that the circulating temperature of fluids during completion is substantially lower than the static temperature. As a result, cements must be able to withstand severe thermal shock when the well is brought into production.

Another important consideration is the inherent fragility and fluid

nature of geothermal formations. Almost every operator expressed a need for lightweight cement slurries, in the range of 1.44 kg/L (12.0 lb/gal) or less, to prevent the occurrence of formation damage and lost circulation.

Information gathered from the operator interviews was also used to design a testing program that would effectively determine whether a particular cement system could withstand the severe geothermal environment and maintain the desired properties during the life of the well. Dowell is primarily an oilfield service company; thus, this project concentrated on the evaluation of cement systems composed of materials commonly available in the oilfield. Most systems were based upon Portland or similar types of cement. By addition of various chemical additives to such cements, the physical and chemical performance can be controlled over a wide range of temperature, pressure, and chemical environments.

For complete evaluation of the performance of candidate geothermal well cements a screening program was designed that involved several key parameters. The program included thickening time, compressive strength, water permeability, bonding strength, expansion, and dynamic exposure testing. Systems that successfully met minimum standards set from the operator interviews were then tested under actual geothermal conditions at facilities located at East Mesa and Niland, California.

Upon completion of testing, six potential geothermal cement systems were selected and submitted to the National Bureau of Standards (NBS) for verification of suitability. All but one are based upon Portland

cement. Three are of normal density while the others are lightweight. The lightweight cements do not perform as well as the heavier systems but meet the minimum requirements.

Some unconventional cementitious systems were evaluated that, while not selected for submission to NBS, deserve mention in this summary. Furan, epoxy, polystyrene and polyurethane polymers were studied briefly. The furan system showed early promise but was eliminated due to thermodynamic instability. Epoxies, polystyrenes and polyurethanes were found to be both practically and economically unsuitable. Portland cements containing microballoons made of glass were shown to be excellent lightweight systems; however, the glass bubbles tend to become reactive at geothermal temperatures potentially resulting in high permeability. Nevertheless, the bubble systems are clearly superior to similar weight conventional systems; however, the considerably higher cost may not be warranted except in the most critical situations.

A basic research program, separate from the screening and testing, investigated the chemistry of calcium silicates, of which Portland cement is mainly composed, in the geothermal environment. This research involved extensive use of x-ray diffraction (XRD), differential thermal analysis (DTA), and scanning electron microscopy (SEM) coupled with energy dispersive x-ray analysis (EDX).

Several significant findings were made in the basic research that should be of value for making further improvements in geothermal well cements.

When cement is to contact highly saline geothermal brines the use of a stabilizing amount of fine silica flour (325 mesh) instead of coarser silica sand is necessary. Highly saline brines depress the solubility of silica and tend to inhibit the entrance of silica into important reactions. Silica flour, by virtue of its high surface area, allows the formation of desired high strength cement compounds such as xonotlite ($6\text{CaO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$).

Other calcium silicate phases have been identified and characterized in this study. Truscottite ($7\text{CaO} \cdot 12\text{SiO}_2 \cdot 3 \text{H}_2\text{O}$), produced by addition of extra silica to the slurry, generally has lower water permeability than xonotlite but shows no improvement in strength or stability. Pectolite ($\text{Na}_2\text{O} \cdot 4\text{CaO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$), a sodium calcium silicate produced by adding an active sodium source to a truscottite type slurry, is very stable to corrosive brines, but is highly permeable. Scawtite ($7\text{CaO} \cdot 6\text{SiO}_2 \cdot \text{CO}_3 \cdot 2\text{H}_2\text{O}$) is produced by exposing xonotlite to carbonates. By itself scawtite is not a good cementing compound; however, in trace amounts it can improve the performance of the cement.

This report, along with those from the other contractors in the DOE sponsored geothermal program*, represents the most comprehensive and

*Colorado School of Mines, Pennsylvania State University, Brookhaven National Laboratory, Battelle-Columbus Laboratories, Southwest Research Institute, and University of Rhode Island.

thorough examination of the geothermal cementing problem undertaken thus far. Perhaps the most significant discovery of this particular study was that Portland cements of normal weight, similar to those already in use at most geothermal areas, appear to be the best that current available cementing technology can offer. This fact should be reassuring to operators who are currently using such slurries. Fortunately, as a result of the screening and chemical studies programs, some promising lightweight systems based upon special modifications of Portland cement have been identified.

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INTRODUCTION

The recovery of geothermal resources requires the drilling of bore holes to depths of up to 6100 m (20,000 ft) into formations with temperatures approaching 370°C (700 F). At some time during the completion of the well, steel casing must be placed to line the hole. Typically the casing is secured with a Portland cement blend similar to those utilized in the completion of oil and gas wells. 1,2,3

The failure of wells in several geothermal fields^{4,5} has been directly attributed to degradation of the cement. This implies that the cementing materials currently used to complete geothermal wells have not been sufficiently evaluated. This report documents a three year research effort performed at Dowell to examine currently utilized cementing systems and develop a superior formulation for the completion of geothermal wells.

Such research was necessitated by the possible consequences resulting from a geothermal well failure. Total loss of control of a well due to cement failure could cost several million dollars and result in fatalities and/or ecological damage. Partial well failures due to inadequate cement can result in energy production declines and environmental damage. Thus, a significant economic and social need has existed for detailed study and development of suitable geothermal cement systems.

Chemistry of Cement Hydration

For a fuller understanding of the problem associated with geothermal

well completions some familiarity with the chemistry of Portland cement hydration and associated phase equilibria is essential.⁶ The following brief resume is submitted.

Portland cement is composed of four major compounds: tricalcium silicate (C_3S)*, beta dicalcium silicate (βC_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). The first two compounds, C_3S and C_2S , comprise about 75% of Portland cement by weight, and their related chemistry largely determines the manner in which the cement performs.

The hydration products of βC_2S and C_3S are $Ca(OH)_2$ and C-S-H gel. The C-S-H gel is of a somewhat variable composition but generally has a high C/S ratio (approximately of 1.3 to 2.4) and has a gel-like structure. It is the principal binder of cement hydrated at ordinary temperature and is the dominant factor governing strength and dimensional stability. The early hydration product of Portland cement even at elevated temperature and pressure is C-S-H gel. It subsequently is subject to metamorphosis at elevated temperature. The alteration products vary depending upon a number of factors. Such alteration is frequently deleterious to strength and permeability. The associated chemistry at elevated temperatures is highly complex and still not fully understood.

*In the abbreviated formulas, C=CaO, S=SiO₂, F=Fe₂O₃, A=Al₂O₃, N=Na₂O, K=K₂O, and H=H₂O.

In the past, as the temperature of oil wells began to exceed a temperature of about 120°C (247 F) serious strength retrogression difficulties occurred. The corrective for the problem, determined empirically by Menzel in autoclave curing of concrete masonry, was a partial replacement of the cement by ground quartz (silica flour).⁷ Later research revealed that the compressive strength vs. silica content correlated closely with the kind of binder formed.⁸ Without silica the C-S-H gel transformed into a highly crystallized and dense phase known as "alpha dicalcium silicate hydrate" (α -C₂SH). Porosity increased and strength decreased markedly. The optimum amount of additional silica was determined to be 30-35% corresponding to a gross C/S ratio of about 0.8. The α -C₂SH did not form; instead, the C-S-H gel reacted to form tobermorite, C₅S₆H₅, a binder of excellent strength. Most of these studies were conducted at 175°C (347 F) over short periods of time, in the order of 7-24 hours. In prolonged curing, as occurs in production wells, pure tobermorite is stable to about 150°C (302 F). Thus from a practical standpoint, the chemistry of calcium silicate hydrate phase transformations is basic to the prediction of long term cement behavior under high temperature downhole conditions.

The compositions of the equilibrium calcium silicate hydrate phases depend largely upon the composition of the initial cement-silica blend, temperature, pressure and time of exposure. Production cements generally have a gross composition of 0.6 C/S (or even lower when silicious extenders are used) to about 1.0 C/S.

In order to illustrate the transformations of the cement-silica mixes

over a broad temperature range only the tobermorite composition, 0.83 C/S, is considered here.

Obviously each transformation is accompanied by new crystallization. In the event strong intracrystal bonds are present, strength may not be affected in either direction. This is generally the case in the tobermorite to xonotlite plus gyrolite transformation. The subsequent transformations are not yet fully understood.⁹ Research on these is currently in progress.

Although chemical reactions and phase transformations are generally acknowledged as the major cause of strength retrogression, evidence also exists that suggests physical changes in the cement, especially relating to the degree of crystallinity, have a profound effect on the integrity of the cement. Some researchers have observed cements that degraded in strength with no apparent chemical changes. For example, J.P. Gallus, et al, reported a cement composition that resulted in the formation of xonotlite.¹⁰ The cement possessed adequate strength initially but degraded severely with time. X-ray diffraction analysis indicated no change in chemical composition; thus, the strength retrogression may have been due to crystal growth of xonotlite resulting in breakage of the multitude of bonds present when microcrystallinity exists. An ana-

logous though not exactly comparable situation is the devitrification of glass with time resulting in brittleness and low strength. Such behavior is much more difficult to control than bulk chemical changes and a great deal of research is necessary to understand and prevent such crystal growth.

In high temperature wells, strength retrogression prevention is primarily achieved by reducing the bulk lime to silica (C/S) ratio in the cement. To accomplish this, silica as α -quartz and/or various silica-rich extenders are used. The most common materials include silica sand (100 μm particle size), silica flour (45 μm), fly ashes, diatomaceous earth, perlite, and bentonite. Results are surprisingly different depending upon which material is employed. Also, specially prepared cements such as API Class J and various lightweight formulations are employed in high temperature cementing.

Cement Placement Technique

Oilwell or geothermal well cementing is basically the process of mixing a slurry of cement and water and pumping it down through steel casing to critical points in the annulus around the casing or in the open hole below the casing string.¹¹ The two principal functions of the cementing process are to restrict fluid movement between formations and to bond and support the casing. In addition, cement aids in protecting the casing from corrosion, preventing blowouts by quickly forming a seal, protecting the casing from shock loads in drilling deeper, and sealing off zones of lost circulation, or thief zones. Figure 1 is a simplified

diagram that describes a typical primary cementing procedure. The slurry is placed so that the casing is completely encircled by a solid sheath of cement. Various methods of cementing geothermal wells have been reported in the literature^{12,13,14,15,16} but detailed discussion is beyond the scope of this report. To achieve a successful cement job, it is necessary to remove the maximum amount of mud from the interval to be cemented, replacing it with cement having adequate strength and bonding characteristics for isolation.

Well cementing encompasses a wide depth and temperature range. Depths can be as high as 6100m (21,000 ft) and temperatures vary from less than 0°C (32 F) in permafrost zones to more than 1100°C (2000 F) in fireflood wells. Obviously a simple "neat" slurry of Portland cement and water is not suitable throughout this wide range. To allow a cement slurry to maintain working properties, service companies have developed cement additives that alter the chemical and physical behavior of the slurry.

1. Accelerators are added to reduce the time necessary for the cement to set and harden. The most common material used for this purpose is calcium chloride.
2. Retarders are used to prolong the set time of cement, and are present in virtually all cement slurries where the temperature in the well exceeds about 60°C (140 F). The most common chemicals utilized as retarders are lignosulfonates, sugars, and borate salts.
3. Extenders are materials which, when added to cement, reduce the density of the slurry. In addition, they increase the "slurry

- yield", or the volume of set product per sack of cement. Extenders are frequently used when pumping past fragile formations.
4. Weighting Agents increase the density of cement slurries. In geopressured areas it is often necessary to render the cement slurry more dense because the bottom hole pressure is greater than the hydrostatic head of a normal weight slurry, 1.8 g/mL (15 lb/gal).
 5. Turbulence Inducers or Dispersants are utilized to reduce the viscosity of a cement slurry. Many additives have a thickening effect upon the slurry. Were it not for dispersants, many common slurry formulations would be unpumpable. Dispersants are generally organic surfactants of a proprietary nature.
 6. Fluid Loss Additives are water soluble polymeric chemicals which prevent loss of slurry water to highly porous or permeable formations. Such additives insure that the slurry will maintain its designed rheological behavior throughout the placement time and that the cement will have enough water to thoroughly hydrate and develop sufficient strength.
 7. Lost Circulation Control Agents prevent loss of the entire cement slurry to highly fractured or weak formations. By adding inert materials to the slurry such as ground coal, cellophane flakes, etc., the "thief zone" is physically plugged and the cement rises up the annulus. Thixotropic cement slurries are also used for this purpose.
 8. Expansion Inducing Additives cause the hardened cement to expand slightly (0.2 to 0.5%). Expansion facilitates a tighter seal between the casing and formations, and dramatically lowers the probability of interzonal communication.

Due to the extensive line of additives available, service companies generally claim the ability to place cement with an adequate thickening time in wells with bottom hole circulating temperatures up to 260°C (500 F). However, retarders in current use can exhibit erratic behavior above 204°C (400 F) and the interaction of retarders with cement at these temperatures is not completely understood. For example, some slurries will set at 232°C (450 F) curing temperature while remaining unset at 288°C (550 F).

Cement systems have been studied for long term stability under static steam at 316°C (600 F).¹⁷ Also, cements from geothermal wells have been analyzed after the fact to determine their chemical composition, with results showing poor cement products. Initial work has been done concerning the basic chemistry of cements at higher temperatures^{18,19}; however, much work has been needed for a comprehensive data base. A cement has been developed exclusively for high temperature well usage²⁰ but its performance in a geothermal environment is unpublished. In spite of this work, no published comprehensive data has existed on cements for geothermal wells.

Lost circulation appears to be commonly associated with geothermal wells. Geothermal formations are inherently porous, highly fractured, or weak. Such conditions require use of lightweight cement slurries coupled perhaps with special lost circulation control additives. Unfortunately the performance of lightweight cements generally suffers dramatically at higher temperatures.

Obviously the difficulties and uncertainties concerning geothermal well cementing have mandated the research documented in this report. Much has been learned during the three year contract term and, like most research, many more questions have been raised. This report should serve as a detailed reference stimulating further research.

ORGANIZATION OF REPORT

This report is arranged in, more or less, chronological order. The research was divided into two major phases:

Phase I - Definition of requirements for geothermal cements and the development of equipment and test procedures.

Phase II - Laboratory and well site evaluation of candidate cement systems.

During Phase I of the research program, the following items were determined by literature review, personal contact with drilling personnel, and on-site study:

1. The expected well life of geothermal wells in different type fields.
2. The expected characteristics for geothermal brines and steams.
3. The static and circulating temperatures expected for the various types of fields.
4. The weight range required for geothermal cement slurries.
5. Typical casing programs for geothermal wells.
6. The minimum acceptable performance criteria for geothermal cements.
7. The bonding ability of cements to geothermal formations and casing.

8. The thermal variations expected during the life of a well.
9. The type of drilling muds expected to be used in geothermal wells.
10. Economic limitations on geothermal completion systems.

At the start of this program it was felt that the lack of precise geothermal cementing knowledge was partially due to inadequate definition of the above parameters. After this information was obtained, the remainder of Phase I was devoted to the design of meaningful tests and test equipment. Most tests were in accordance with American Petroleum Institute (API) standard procedures but adjustments were occasionally made due to the specialized geothermal environment. Much of the equipment required for evaluations performed in Phase II was already on hand, but special simulations and use of the equipment were defined in Phase I. During Phase I, Dowell also arranged for the use of geothermal wells for onsite testing.

After establishing procedures, parameters, and equipment in Phase I, Phase II evaluated three critical parameters of three types of cementitious systems. The systems were: 1) Portland cement and modified Portland cement systems, 2) synthetic silicate and/or aluminate systems, and 3) organic-based "polymer" systems. The critical parameters were: 1) stability measurements, 2) placement measurements, and 3) chemical measurements.

All of the candidate cementitious systems were evaluated in relation to several parameters including compressive strength, placement ability,

permeability, and long term stability. Minimum quantitative standards concerning these evaluations were determined during Phase I.

Stability measurements were conducted at the highest expected temperatures. Strength and permeability profiles were determined along with x-ray diffraction (XRD), scanning electron microscope (SEM) and differential thermal analysis (DTA). Also, selected samples were examined by energy dispersive x-ray analysis (EDX). Such analytical tools give detailed knowledge concerning the chemical and physical nature of a cement system.

Following laboratory scale evaluation of proposed cement formulations, promising systems underwent further evaluation upon exposure to actual geothermal conditions in wells located at Niland and East Mesa, California. Results were then compared with those from the laboratory simulations.

Extensive chemical and instrumental analysis of the cementitious formulations was performed as a basic research effort to better understand the chemical interactions that cement undergoes internally and externally in a geothermal environment. X-ray diffraction, SEM, and DTA were utilized extensively.

Results from all testing efforts were collated and the best formulations were selected for submission to the National Bureau of Standards (NBS) for verification of their suitability as cements in geothermal wells. Possible directions for further research in this area are also discussed at the conclusion of the report.

PHASE I

During the period May 1, 1977 to September 30, 1977, background information on high temperature cementing and related problems was gathered. Many publications on high temperature cementing were studied, and Dowell proprietary research findings and cementing records were reviewed.^{11, 17, 21, 22} 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 definition of current cementing practices and problems and helped set objectives for research. Initial test procedures were then designed based on findings from the study.

Variables to be determined during the Phase I study included the following: (1) expected well life in different type fields, (2) expected characteristics of fluids, (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, (7) economic limitations on completion systems, (8) minimum and/or acceptable strength for cement, (9) desired and/or acceptable porosity and permeability of cement, (10) heat transfer properties of cement, and (11) desired and/or acceptable cement bonding strength to pipe and rock.

INFORMATION GATHERED IN OPERATOR INTERVIEWS

1. Wells are rarely cemented under geothermal conditions. Maximum fluid circulating temperatures, where measured, seldom exceed 116°C (240 F). Mud flow line temperatures are 93-104°C (200-220 F).

2. Drilling programs of all the operators responding to our questions call for setting surface and production pipe above the reservoir. 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 difficulty. This is thought to be in the 116°C (240 F) range although the operator did not have a precise measurement.
3. 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.
4. 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 H₂S. 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 that of sea water are reported. Pressures are seldom above hydrostatic except in geopressure zones. Dry steam fields report measured reservoir pressures that vary from 3,500 to

3,800 kPa (500 to 550 psi) at depths from 900 to 3,000 m (2,950 to 9,840 ft). In hot water fields, pressures at the bottom of a 3,000 m hole will be less than 3,500 kPa. Reservoirs appear to be slightly under pressure relative to hydrostatic in some fields. Exceptionally high pressures of 69,000 to 138,000 kPa (10,000 to 20,000 psi) have been reported for geopressed zones which are found from 3,700 m (12,000 ft) to over 6,000 m (19,700 ft) deep. Bottom hole static temperature and bottom hole circulating temperature data are often unreliable and misleading. Published reservoir temperatures vary by as much as 66°C (120 F) 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 exuberance on the part of the authors. The operators themselves use different methods to measure temperatures with results that vary by as much as 10°C (18 F) for the same well. The highest accurately measured temperature reported to us is 357°C (675 F). One well was reported to be higher, but all others were less than 316°C (600 F). Thermal shock effects on cement may be significant. All operators expressed concern over the cement to pipe bond, when subjected to temperature cycling as a result of drilling, testing, shutting in, and producing. In feasible areas wells are left on a bleed system to maintain temperature, 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.

INFORMATION PROVIDED BY COMPANIES INTERVIEWED

Information gathered from companies operating geothermal wells by a series of contacts by mail, phone, and interviews with drilling personnel is listed here. Most of the companies were very cooperative although some provided significantly more information than other. Some of the companies utilized consultants for drilling and completion guidance and therefore had little information on cement problems. Usually we were referred to the service companies who performed the cementing for information concerning 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 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 protect anonymity but it was preferred by most of the companies.

"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 production over a longer time may be possible. Wells may decline in production from formation plugging. This operator believes that the wells can be revitalized but no attempts have been made as yet. No wells have been lost from cement failures.

Cement formulation used:

Class G, 1:1 perlite

40% silica flour

3% gel

Retarders, friction reducers

On surface pipe, 1.52 kg/L (12.7 lb/gal) slurries were used, and 1.87 to 1.92 kg/L (15.6 to 16.0 lb/gal) neat G plus 40% silica flour was used on the production string. Use of as light a slurry as possible is preferred because of a low fracture gradient. No correlations have been

noted between cement density and stability. Two to three hours of pumping time, including a 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 the steam after initial flow begins. Fifteen percent of the fluids are reinjected. These fluids could be used to mix cement but are probably unnecessary as other sources are available.

Temperature

Reservoir temperature is 246-249°C (475-480 F) in dry steam fields as measured by wireline logging tools. The mud flow line temperature is usually 104°C (220 F) when drilling near the reservoir. Downhole circulating temperatures are 150°C (300 F) maximum and can be lowered by circulating before cementing.

Depths vary from 1,500 to 3,000 m (4,900 to 9,840 ft) and maximum pressures are 3,500 kPa (500 psi) for dry steam and hydrostatic for other parts of the field.

Thermal Variations

Temperatures to which the cement sheath is subjected will vary by 93°C (170 F) during drilling and completion. Temperature for production

string cements will increase from 116 to 204°C (240 to 400 F) during WOC (waiting for cement to set) time. During testing and production a temperature change of 150 to 232°C (270 to 420 F) in less than one hour may occur resulting in fractured cement. The maximum temperature encountered was 254°C (490 F) in dry steam fields, and 288-316°C (550-600 F) 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 produce mud but otherwise does not present a problem. This company would be willing to change muds to improve cement jobs.

Casing Programs

Usual casing practice is to cement 150 m (500 ft) of 20 in. conductor to surface, followed by up to 760 m (2,500 ft) 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 or at least minimizes casing elongation. The 9-5/8 in. producing string is set above the reservoir by either hanging at approximately 700 m (2,300 ft) 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 hydrazine is occasionally used as a flush.

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

Minimum Strengths

For Class G, 1:1 perlite plus 40% silica flour, 7,580 kPa (1,100 psi) within 24 hours is needed. For neat G and silica flour, 15,860 to 16,550 kPa (2,300 to 2,400 psi) after 8 hours is required. This company would welcome systems that develop higher strength.

Porosity and Permeability

No specific data is available concerning 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 this to be 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 that 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 will probably cause failure of the cement-pipe bond in some cases. Casing does not elongate if properly cemented. Special care is taken to complete the cement sheath from surface to total depth. All wells are placed on a 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. The cement system normally pumped is a 1:1 Class G: perlite system containing 35 percent silica flour, 2 to 3 percent bentonite gel, and up to 0.5 percent friction reducer. 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. The only problem expected will be an occasional sand inflow that will require removal.

Fluid Characteristics

Reservoirs are in low salinity brines (2,500 to 3,800 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. Use of reservoir fluids as mix water is unnecessary because other sources are available. Spent fluids are reinjected.

Temperatures

Precise reservoir temperatures are classified, but low salinity fields vary from 177 to 204°C (350 to 400 F). Higher salinity fields are over 204°C. These temperatures are measured by wireline logging instruments. Bottom hole circulating temperature is not measured, but probably does not exceed 104°C (220 F). All wells can be cooled by circulating. Mud flow line temperatures are less than 93°C (200 F). Depths vary from 1,200 to 2,100m (3,900 to 6,900 ft) and pressures are hydrostatic.

Weight Range

Slurries are adjusted to 1.44 to 1.56 kg/L (12.0 to 13.0 lb/gal). This company would like to use 1.2 kg/L (10.0 lb/gal) 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 (170 F) are expected. When undergoing tests, a well can cycle from 93°C to over 204°C (370 F) in less than one hour. When shut in, cooling occurs at a lower rate. This company believes 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 to both simplify procedures and abide by environmental restrictions. Mud costs can approach \$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 (100 to 200 ft) 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 (2,500 ft). 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 are placed every 120 m (400 ft). 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. This liner 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.

Porosity and Permeability

Data was not available.

Heat Transfer

Heat transfer properties of cement are not considered important.

Bonding

This company believes that bond of cement to pipe is good and will hold with time. Variations in temperature will not cause bond failure. Cementing of the 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 the pipe will not elongate and the 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 with a 1:1 Class B:perlite system containing 40 percent silica flour, 2 percent bentonite gel, 0.5 percent dispersant, and 1 to 3 percent retarder.

Weight Range

The weight range of slurries now in use is 1.57 to 1.63 kg/L (13.0 to 13.6 lb/gal). 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, 1,500 ppm TDS. The 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° (400 F) as measured by a wireline logging tool. Mud flow line temperatures are as high as 93°C (200 F). Wells may flow while drilling. Depths range from 305 to 915 m (1,000 to 3,000 ft) and pressures are hydrostatic.

Thermal Variations

During drilling, temperature changes of 93°C (170 F) are possible in a few hours. Under testing, wellbore temperatures can change 93°C to 204°C (370 F) 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 required. They emphasized a need to clean the well with a spacer or wash before cementing.

Company D"Well Life

The longest period a well has been in use is seventeen years. In one area fifty percent of the wells required no additional work after completion. The rest required squeeze cementing and some casing replacement. The average well age is 12 years 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 analysis 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 insufficient time has elapsed for evaluation of effectiveness. Laboratory studies indicate probable strength retrogression with time. Recently drilled wells in this area have been cemented with a 1:1 Class G:perlite system containing 40 percent silica flour, 2 percent bentonite gel, 0.5 percent dispersant and up to 1 percent retarder. The slurry density is 1.46 kg/L (12.2 lb/gal).

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. An analysis of the noncondensable gases is given below.

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

Hot water and brine fields have percentages of dissolved solids that range from fresh to extremely saline.

Temperature

Reservoir temperatures vary from 177 to over 371°C (350 to +700 F). 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 (464 F). Most hot waters are less than 260°C (500 F), but one is 399°C (750 F), determined from a single one measurement during which the logging tool (rated to 399°C maximum) broke. It is not known whether the device broke due to heat or from other causes. Circulation temperatures vary between 93°C (200 F) and 204°C (400 F) depending upon whether the measurements are taken in the reservoir or above it. Mud flow line temperatures are usually 82°C (180 F). Downhole temperatures can be lowered by circulating before cementing.

Slurry Weight Range

Cement slurries currently used vary from 1.52-1.68 kg/L (12.7 to 14.0 lb/gal). Because of the low formation pressures and low fracture gradients in most reservoirs, weights as low as 1.12 kg/L (9.3 lb/gal) would be ideal. No correlation has been noticed between cement weight versus stability.

Thermal Variation

During drilling and completion of a well, the temperature variation is probably less than 93°C. However, when a well is tested the casing and cement are subject to a temperature change at 149 to 204°C (300 to 400 F) during the testing period of 6 hours. 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, 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 vary depending on the field. Tuffs, andesite, basalt, serpentine, sandstones, shales and graywacke are most commonly encountered.

Economic Limitations

Casing programs now in use vary with fields but usually include 30 to 150 m (98 to 490 ft) of 20 in. conductor cemented to surface, 305 to 760 m (1,000 to 2,500 ft) of 13-3/8 in. surface pipe cemented to surface, and 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 6,890 kPa (1,000 psi), but 689 kPa (100 psi) after 25 years of service is acceptable. Cements now in use are 20,685 kPa (3,000 psi). Inadequate data are available to estimate downhole strengths of cements now in use.

Porosity and Permeability

Little information is available, but data from wells which failed after five to seven years of service indicate a permeability to gas of no

more than one millidarcy (md) after 25 years. Heat transfer properties of cement are not considered important by this operator.

Bonding Strength

Information concerning bonding to pipe or rock is inconclusive at this time. This operator believes that variations in temperature cause failure of the cement to pipe bond. Casing elongates as much as 0.76 m (30 in.), while the cement sheath does not elongate at all. Expanding cements may be desirable. Cement bond logs have been performed but appear to be inconclusive.

INITIAL TESTING PROGRAM

The testing program for possible geothermal cement systems was designed to be comprehensive and discriminating. As a result, literally hundreds of compositions were involved and will be described in detail later in the text. For each of these compositions several tests were required for a complete evaluation. To minimize the total number of tests and avoid unnecessary and redundant evaluations, a screening program was devised to quickly identify unsuitable systems and save more complicated and time consuming tests for systems which showed promise. A block diagram of the screening procedure is shown in Figure 2.

For any cement system to be seriously considered for suitability in a downhole environment, one must first be certain that the material can be successfully placed in the well. Thus, a thickening time test was the first step in the screening process. Thickening time is defined as the

length of time a cement slurry can be pumped before it reaches a viscosity beyond which pumpability is impossible. These tests were performed using high temperature-high pressure consistometers according to a standard procedure dictated by the American Petroleum Institute (API).²³ The consistometer continuously stirs the cement slurry while exposing it to a simulated wellbore environment. Resistance of the cement to stirring is continuously monitored. For this program the tests were run at 150°C (300 F) and 36,000 kPa (about 5,000 psi) pressure. Systems that could not be pumped for at least three hours under these conditions were immediately dropped from consideration.

Systems that survived the thickening time evaluation were next subjected to compressive strength tests. The test procedure conformed to API specifications.²⁴ Candidate cement slurries were cured at 225 and 325°C (440 and 600 F). The minimum acceptable standards for strength development were 3,500 kPa (500 psi) within 24 hours and 7,000 kPa (1,000 psi) within 7 days of curing.

Cement compositions that exhibited satisfactory compressive strength development were next evaluated as to water permeability. In many cases permeability is more critical than compressive strength because a highly permeable cement cannot effectively isolate producing zones. In a highly fluid geothermal environment, cement with low water permeability is essential. As usual, standard API procedures were followed during the permeability evaluation.²⁵ Maximum acceptable permeabilities varied depending upon the density of the cement slurry in question.

Realistically, a low density slurry cannot be expected to be as impermeable as a higher density composition. Thus, the systems were divided into two groups: normal weight (greater than or equal to 1.8 kg/L or 15 lb/gal) and light weight (less than 1.8 kg/L). The maximum allowable permeabilities for the light and normal weight systems were 0.25 and 0.10 md, respectively.

The next test for the surviving cement systems was a bonding test. This evaluation was designed to determine how well the cement bonds to solvent-cleaned smooth surface pipe. Two-inch pieces of lathe surfaced pipe were placed in the center of standard two-inch cube molds, and cement slurry was poured into and around the pipe.

After 28 days of curing under water at 204°C (400 F) and 17,500 kPa (2,500 psi) the molds were removed from the curing chamber or autoclave and cement bonding was visually determined without stripping the molds. The first bond strength measurement determined the force necessary to break the cement/steel bond in the interior of the pipe. A Tinius-Olson compressive strength testing instrument was used to punch the cement "core" out of the pipe. Next the cement/steel bond to the outer surface of the pipe was measured. Bond strength was calculated by dividing the total force necessary to break the bond by the surface area of the cement/steel interface. The minimum acceptable strength was 690 kPa (100 psi).

Following the bond tests the cement systems, which by now had shown considerable promise, were tested for degree of expansion upon curing.

A limited amount of cement expansion can be very beneficial in that it facilitates intimate bonding of the cement to both the pipe and formation. Because the apparatus specified by the American Society for Testing and Materials (ASTM) is not designed for high temperature and pressure,²⁶ a special expansion sleeve was developed for this project that enables measurement of expansion of cement cured at simulated downhole conditions. The sleeves, illustrated in Figure 3, are constructed of stainless steel having essentially the same coefficient of expansion as cement.

The test slurries are poured into the sleeves and placed into autoclaves for the desired curing period. Expansion is measured as a change in circumference at the pins and converted to linear expansion relative to the diameter. This method has a distinct advantage compared with the ASTM bar method²⁷ in that there is no ambiguity as to exactly when the cement has set. The ASTM method requires the use of bars that are removed from molds when the cement has just set. Much of the expansion could be undetected if the bars are not removed at precisely the moment of setting. Because the cement never leaves the sleeve in our method, a measurement of total expansion is guaranteed.

The remaining candidate cement systems were cured in the sleeves at 204°C (400 F) and 17,250 kPa (2,500 psi) for 7 and 28 days. The cements were expected at the very least to be dimensionally stable (i.e. 0% expansion). On the other end of the spectrum, expansion greater than 1% was considered excessive.

The sleeves performed very well throughout the test program. Reasonable care is dictated when measuring changes in sleeve circumference; thus, a micrometer accurate to 10^{-4} in. is required.

The final step in the screening program was an erosion test to determine the effects of dynamic steam and brine contact. Any system that exhibited tendencies of sloughing was considered unstable and rejected. To accomplish such testing, a geothermal simulator was designed and constructed. The apparatus was named the Dynamic Brine Exposure Testing Apparatus (D-BETA). A schematic diagram of the D-BETA appears in Figure 4.

The D-BETA is a recirculating system in which a synthetic geothermal brine flows past up to 32 one-inch diameter cylindrical cement specimens. The rate of flow is controllable and the brine may be heated to 350°C (660°F) with pressure up to 21,400 kPa (3,100 psi). The composition of the brine, given in Table 1, is typical of those found in moderately saline wells in Southern California.²⁸ After exposure to the brine for specified periods of time, ranging from 28 days to 15 months, the cement cores were removed and examined.

High temperature brines are extremely corrosive. Thus, most of the D-BETA was fabricated with Inconel 600 alloy. Nevertheless, deterioration of seals and scaling was a chronic problem. As testing continued, however, these problems were solved and data gathering was not seriously hampered. As a safety consideration, the D-BETA was placed in an enclosed location well away from the laboratory. Performance of the system was continuously monitored by remote control.

FIELD TESTING

Cement systems that survived the screening program were then slated for dynamic testing under actual geothermal conditions in wells located at East Mesa and Niland, California. A map showing the locations of these wells is found in Figure 5. The brines to which the cements were exposed ranged from moderately saline at East Mesa to extremely saline at Niland. Brine compositions are listed in Table 2.

The testing apparatus of East Mesa is very similar to the D-BETA in basic design. The field apparatus differs in that it is possible to isolate each cell from the brine circulation allowing for convenient sample removal. The temperature of the brine is about 150°C (302 F) and does not recirculate; instead, one pass is made through the cells and then flashed to the atmosphere. As can be seen in Fig. 6, a photograph of the apparatus, the brine flows from the well into a 25 gallon surge tank. Then, the brine passes through the sample cells which, like the D-BETA, are made of Inconel 600 alloy steel, and finally to disposal.

At Niland, the test procedure was much simpler. Because of the extreme salinity of the brine, scaling was a chronic problem and the well had to be shut down periodically to restore circulation. Thus, a circulating design used at East Mesa was deemed unsuitable. The cement samples were placed in a wire basket that was bolted inside one of the flashers. Exposure to a flashing brine as corrosive as that found at Niland was a particularly rigorous test.

INSTRUMENTAL EVALUATION

Many cement systems underwent detailed chemical analysis during the screening and field testing program in an effort to find an explanation for observed behavior. This was done using the following techniques as previously mentioned: XRD, DTA and SEM. Occasionally some emission spectographic and plasma emission spectographic analyses were performed to aid in identification of certain silicate phases and to determine trace element substitutions.

These analytical techniques are well known and established; however, when dealing with materials as impure and inhomogeneous as cement, special sample preparation is necessary. The greatest difficulty lies in obtaining a representative sample of the binder. Generally, techniques similar to those used in geochemical analysis of mineral specimens are followed.

X-ray diffraction analysis is the most informative instrumental technique in cement research. A positive identification of the various calcium silicate hydrates and auxiliary phases is readily obtained. Some expertise is necessary, however, to correctly identify some of the calcium silicate hydrates because they have very similar crystal structures and share many characteristic diffraction peaks. When preparing cement specimens for X-ray analysis, it is important to use a representative cross-section of the whole. Material exposed to external conditions must be mixed with cement at the interior of the specimen. The cement is thoroughly dried with acetone, degassed and ground in a ball mill to pass a No. 200 sieve.

State of the art x-ray equipment was used in this investigation. The cement was exposed to Cu radiation ($\lambda = 1.54 \text{ \AA}$) at 40 KV and 20mA. A high precision vertical goniometer with a reading accuracy of $< 0.002^\circ$ 2θ was utilized with a scintillation counter as detector. Solid state electronics, including a pulse height selector and linear ratemeter, were connected to both a chart recorder and computer system for versatile data acquisition.

Much of a set cement is largely amorphous and thus is not detectible by XRD. Common examples would be amorphous silica, C-S-H gel, and non-crystalline calcium hydroxide. To detect such phases and monitor thermodynamic behavior, differential thermal analysis (DTA) was performed. DTA indicates the degree of hydration of amorphous materials which are not easily detectable by other methods.

DTA technique involves heating a sample at a constant rate, usually 10°C per minute, and monitoring endothermic and exothermic reactions that the sample undergoes. For example, at approximately 550°C , Ca(OH)_2 decomposes with an accompanying endotherm. Such a reaction is very characteristic of Portland cements cured at low temperature. It is possible to follow hydration of cement slurries by DTA whereby samples are analyzed at various times as hydration progresses. The resulting thermograms will show the quantitative state of most reactive materials in the cement. Other phenomena that can be monitored include the effects of retarders on cement hydration and long term behavior of aged cement samples.

The mechanics of DTA involves differential heat sensors to detect reactions in test samples in comparison to an inert reference material (usually Al_2O_3). Samples are usually ground to pass a No. 100 sieve and are washed with acetone and dried in vacuum to stop hydration. The instrument used in this study uses 25 mg samples and can be programmed to heat to $1,250^\circ\text{C}$. Platinum sample holders and platenel thermocouples are required.

SEM is a valuable research tool in cement research. Observation of the microstructure and concurrent electron microprobe analysis yield helpful information to explain the physical behavior of cements. Sample preparation of cements for SEM is a critical step in obtaining useful information. There are basically two stages involved: (1) proper sample drying and mounting, and (2) coating the sample with conductive material.

In the first stage small chips of cement are placed in a vacuum oven and heated to about 95°C to remove free water. After initial drying the chips are crushed to less than 0.25 cm^2 in cross-sectional area. Careful selection is necessary at this point to assure that the chips to be analyzed are representative of the cement system. A chip is glued onto an aluminum stub with Duco cement. The mounting is then placed in a drying oven at 110°C to remove all water and gases from the sample and glue.

A thin coating of carbon and gold/palladium alloy is necessary because cement is a non-conductive material. An escape route or ground is

necessary for the electrons that bombard the surface of the sample. The coating is applied by vapor deposition in a vacuum evaporator and is usually no thicker than 700 Å.

PHASE II

Phase II covered the period October 1, 1977 to July 31, 1980. During this time hundreds of tests were performed on over a hundred candidate cement systems. Discussion of each system in this report would be impractical because many yielded negative results. Therefore, only the most significant results that serve to characterize the behavior of each basic cement category will be reported here. Those interested in minute details are referred to the series of quarterly progress reports that were submitted throughout the contract term.²⁹⁻³⁶

This section is divided into six principal parts. The initial screening program is discussed first, followed by results of the tests run in the D-BETA and at East Mesa and Niland. The limited evaluation of polymer cements is next. From these results the final selection of recommended systems was made and is discussed in detail. Last, the chemical studies program is covered.

CANDIDATE GEOTHERMAL CEMENTS

In general, this investigation was limited to materials that are currently readily available in the oilfield. Some rather exotic systems were evaluated as part of the chemical studies program, discussed separately, but other subcontractors in the Brookhaven program experimented with more unusual formulations. With few exceptions, Dowell's efforts were concentrated on cementitious materials based upon calcium silicate hydrates.

The most extensive group of candidates was based upon silica stabilized Portland cement. Three types of Portland cement, API Classes B, G, and H,³⁷ were evaluated using various extenders, dispersants, retarders, etc. that will be discussed in detail later.

Several types of non-Portland cement were thoroughly tested. API Class J (tentative designation) cement is a special formulation especially for use in high temperature wellbore environments. Class J is basically a mixture of $\beta\text{C}_2\text{S}$ and quartz such that the C/S ratio is 0.83. Recalling the previous discussion of cement chemistry, the C/S ratio of 0.83 corresponds to a normal Portland cement stabilized with about 35 percent silica. Also the absence of fast hydrating C_3S allows placement in many cases without adding retarders. Class J was evaluated with many of the same additives used in the Portland cement evaluation.

Some commercially prepared lightweight cements were evaluated as potential geothermal binders. These cements are essentially Portland cements that have been premixed with a low density silicious aggregate material. Blends of pure lime (CaO) and silica at $\text{C/S}=0.8$ were also tested. Another modified Portland cement that was evaluated is called "slag cement." Slag cement is a normal grind combination of Portland cement and special blast furnace slag with normal water requirements.

As discussed in the introduction, many additives for cement slurries are used to modify performance. Because geothermal wells are of high temperature and the formations are typically fractured and weak, the use of

retarders and extenders is almost mandatory. The most commonly used retarders include chemicals that fall into two categories: lignosulfonates and modified sugars. Such chemicals, usually added between 0.1 and 3.0 percent by weight of cement, slow down hydration of cement particles and allow adequate placement time. Both types were used extensively in this program.

Extenders comprise a much more diverse group of materials. Generally, extenders are of lower density than the cement and thus allow substantial reductions in slurry density. Due to some rather complex chemical interactions that occur in cements at elevated temperatures, one must be careful when choosing an extender for a geothermal well cement.³⁸ In this investigation, the following extenders were evaluated: (1) bentonite (gel), (2) perlite, (3) fly ash, (4) diatomaceous earth, (5) coal, (6) gilsonite, and (7) sodium silicate. Bentonite and sodium silicate extend slurries by hydration, requiring substantial increases in water addition; the other materials achieve extension by purely physical means.

In some wells addition of NaCl or KCl to the cement slurry is necessary. If cement is pumped past a soluble salt formation, a fresh water based slurry will tend to dissolve the formation resulting in a poor bond. Salts can be added from 3 percent by weight of water to 37 percent or a saturated solution.

The only non-silicious cement system that was thoroughly investigated in this study was based on mixtures of furfuryl alcohol and ground coal.

A 50:50 mixture of furfuryl alcohol and partially polymerized furfuryl alcohol (Quaker Oats Experimental Resin No. 4607) was blended with coal of a particle size to pass through a No. 20 sieve. ZnCl_2 is a catalyst for the solidification of the system and the thickening time is controlled by varying its concentration.

INITIAL SCREENING PROGRAM

The initial screening program, described in the preceding section, was the most comprehensive and time-consuming task in this project. Table 3 lists the systems that, collectively, indicate the general behavior of each category of candidates. Table 4 is a compilation of results of the screening tests for each system.

API Classes G and B Portland cements were extensively tested under geothermal conditions in the screening program. In general, Class G systems performed better than their Class B counterparts. Both Portland cements were superior to most non-Portland materials.

Water permeabilities were generally less than 0.1 md indicating a dense structure. No tendency was detected for micro-cracking resulting from test conditions or shock stresses during sample removal and preparation. Compressive strength data have been plotted in Figure 7 for convenience of examination. The plots show the expected strength cycling that occurs upon extended curing due to cement phase transitions and recrystallizations. The minimum of the strength profile corresponds to the disruption of structure upon transition. With further curing strength may

be recovered. Generally, recovery was faster in systems cured at 316°C.

All of the normal weight Class G systems (Nos. 1,2,3,5,6,7 and 8) performed satisfactorily, with Systems 2 and 3 performing best. Both exhibited excellent strength and extremely low permeability. System 3, containing Needles fly ash, exhibited the highest outside bond strength of all systems in the screening series.

Normal weight Class B systems (Nos. 49,50,52 and 53) were not as successful. System 49, stabilized with 35 percent silica sand, exhibited poor long-term strength at 227°C. In addition, outside bond strength to steel pipe was unacceptable. System 50, with 35 percent silica flour, fared much better. Systems 52 and 53, containing 20 percent NaCl and KCl, respectively, were also excellent performers.

Although the normal weight systems were generally acceptable, the real interest lies with the lightweight slurries. The lightweight Class G systems (Nos. 4,9,10,11,12,13,14 and 15) showed mixed performance. Those above 1.6 kg/L (13.5 lb/gal) were satisfactory. Lighter systems were unacceptable, usually due to low compressive strength. The best lightweight Class G system was No. 11, containing gilsonite.

Only two lightweight Class B systems were evaluated (Nos. 51 and 54). Both were marginally acceptable as to compressive strength; however, they performed well in subsequent tests though not as well as their Class G equivalents.

Candidate systems based upon API Class J cement (Nos. 16-33) were not as successful as the Portland group, but three individual cases looked promising (Nos. 17, 22 and 31). The acceptable systems were of normal weight. Two lightweight systems (Nos. 28 and 30) performed acceptably as to strength and permeability but were dropped when they exhibited little or no bonding strength to steel.

It is interesting to note that the successful Class J systems closely paralleled the acceptable Portland-based cements. Again, the addition of Needles fly ash appears to be beneficial. Systems containing diatomaceous earth (Nos. 18, 19 and 20) were dropped due to unacceptably short thickening times despite large additions of retarder. The candidates containing Airox pozzolan (Nos. 23, 24 and 25) were also unresponsive to retarders. Sodium metasilicate cannot be used with Class J because it imparts high permeability (No. 33) and low strength at 316°C.

Four high alumina cement formulations, utilizing Ciment Fondu, were tested (Nos. 34-37). A combination of retarders R1 and R2 was required to obtain an acceptable thickening time. Systems 34 and 35 were acceptable as to strength but were slightly too permeable. Because they were borderline in performance, these systems were allowed to pass to the next stage of evaluation.

Of the systems based upon slag cement (Nos. 38-41), only one failed to meet minimum standards. The unacceptable system (No. 40) was, not surprisingly, the lightest in density. Containing sodium metasilicate,

No. 40 was dropped due to low strength. System 39, containing Needles fly ash, suffered a severe strength loss between one and seven days; however, strength never dropped below minimum. Permeability and bonding performance was excellent.

All of the lime/silica systems (Nos. 42-48) except one (No. 42) had unacceptably low compressive strength and were dropped as candidates. Despite the adequate strength of No. 42, a very light 12.0 lb/gal slurry, its permeability was unacceptably high. As a result, none of the lime/silica systems survived.

Commercial lightweight cement systems, utilizing TXI Lightweight (Nos. 55-60), did not survive the initial screening program. All of the systems were of very low density and exhibited extremely poor strength.

To summarize, the Portland cement compositions performed well in the initial testing as long as silica had been added to adjust the lime to silica ratio to one or less. Silica flour (45 μ m particle size quartz) was the best source of additional silica. Some pozzolanic materials which should act as sources of silica failed at 316°C (600 F). These were certain fly ashes, impure diatomaceous earths, and heated shale. Such problems with pozzolans in Portland cement have been previously reported.^{17,39,40} Increasing the water content of the cement by using light-weight additives reduced the strength and increased permeability as expected.

The Class J and lime-silica systems performed much like similar weight Portland slurries. The lime-silica compositions required extra mixing water to produce a pumpable slurry and were less than 1.56 kg/L (13.0 lb/gal) in density.

The high alumina cements had lower strength and higher permeability than similar weight calcium silicate systems. Addition of silica flour resulted in higher strength but unacceptably high permeability. Lightweight aluminate systems deteriorated rapidly and thickening times were unpredictable above 125°C (260 F).

Commercial lightweight cements performed acceptably to about 215°C (420 F). At 316°C (600 F) strength dropped and permeability increased well beyond acceptable limits. Slag cements performed somewhat better, but addition of some fly ashes resulted in deterioration. The chief disadvantage of slag cement is the release of noxious and corrosive sulfides at geothermal temperatures.

X-ray diffraction analysis was performed on candidate systems which had been cured at 316°C for 28 days. The results appear in Table 5. Xonotlite was the dominant principal phase in the Portland, lime-silica and slag cement formulations, with calcite often occurring in small amounts. Occasionally tobermorite appeared as a principal phase (Nos. 3, 39, 47, 54). Except for No. 47, the tobermorite-bearing systems contained fly ash. Fly ash contains a large amount of aluminum oxide, a material known to stabilize tobermorite to 250°C.⁹ This data implies that tobermorite can be stabilized to higher temperatures; however, with

extended curing, recrystallization to xonotlite could take place. The presence of calcite indicates that the geothermal brine attacks the cement, replacing silica with carbonate. Upon extended curing, complete replacement could conceivably occur.

Class J systems almost invariably contained the phase scawtite, a carbonated calcium silicate hydrate similar to xonotlite, instead of calcite. Why scawtite does not appear with Portland systems is not clear. The high alumina cements formed various calcium aluminosilicate hydrates as binding phases.

DTA thermograms of the screening program samples cured for 28 days at 316°C (600 F) are shown in Figure 8 for the readers' further study. A cursory examination of the thermograms reveals the reactivity of samples after removal from curing conditions. If an endotherm appears near 100°C, it is likely that additional hydration has occurred at a temperature lower than that of curing. Such behavior should be noted and kept in mind as x-ray data is evaluated.

Exotherms are usually associated with the presence of carbonaceous residues from fly ash, coal or gilsonite. The ability to detect such materials in addition to amorphous cement phases by DTA can be useful in the characterization of cement systems. Plot 54 is an example of a cement system utilizing a fly ash which was almost completely void of carbonaceous material. No distinctive exotherms are evident in the 400- 600°C range. System 3, however, shows evidence of a carbonaceous fly ash.

It is interesting to note that none of the samples contained Ca(OH)_2 , which is detected with DTA by an endotherm at 550°C . The presence of Ca(OH)_2 is often accompanied by strength retrogression. Silica added to these systems effectively removes Ca(OH)_2 and prevents formation of $\alpha\text{-C}_2\text{SH}$.

Endotherms near 800°C are usually associated with carbonate decomposition. Such behavior, followed by a sharp exotherm at 850°C , was noticed with Class J, slag cement, and lime-silica systems. The endotherm is most likely associated with low lime C-S-H gel.

SPECIAL ADMIXTURES

A series of tests was conducted to determine the compatibility of several candidate geothermal cement systems with special admixtures such as fluid loss additives, dispersants and retarders. Thickening time, compressive strength, fluid loss and permeability tests were conducted. Table 5 lists the composition of the special slurries and Table 6 lists the test results.

As seen in Table 6, thickening time was generally not a problem. For these tests a modified API Schedule 30 was used with a bottom hole circulating temperature (BHCT) of 150°C (300°F) and a pressure of about 36,000 KPa (5200 psi). In most cases the combination of retarder with fluid loss additives and dispersants tends to increase the thickening time beyond that which is measured when the retarder is present by itself.

Fluid loss control was not good in the saturated salt system S-6 and the highly extended system S-5. Addition of a greater amount of fluid loss additives would probably reduce fluid loss to an acceptable level.

The effect of additives upon permeability can be determined by comparing data in Tables 4 and 7. For example, System S-3 had a water permeability of 0.09 md; without fluid loss additive (Table 4-System 4) the permeability was 0.05 md. A permeability of 0.1 md was measured on System S-4 while without fluid loss additive (Table 4-System 9), 0.06 md was determined. This type of behavior suggests that fluid loss additives do not restrict flow through a solid matrix, only in unhardened slurry.

Compared with data obtained in the screening program, it appears that the special admixtures can enhance strength development. System S-1 had 52,400 kPa (7,600 psi) compressive strength at one day. Without fluid loss additive (Table 4-System 2) the same basic system had a strength of 24,200 kPa (3,500 psi). At 28 days S-1 had a compressive strength of 25,000 kPa (3,630 psi) and 18,600 kPa (2,700 psi) without fluid loss additive. System S-3 had 10,800 kPa (1,560 psi) at 28 days compared to 5,350 kPa (775 psi) without fluid loss additive (Table 4-System 4). A significant decrease, however, was noticed with Sample S-6 which had a strength of 18,550 kPa (2,690 psi) at 28 days, but without fluid loss additive, a strength of 30,200 kPa (4,380 psi).

SIMULATED GEOTHERMAL TESTING

As the initial screening program neared completion, surviving cement systems underwent evaluation under simulated geothermal conditions. The

principal apparatus used in this study, the Dynamic Brine Exposure Testing Apparatus (D-BETA), is described in the Phase I section of this report.

The D-BETA was initially tested for two weeks at 150°C(300 F) and brine circulating rate of 0.12 L/min. The composition of the brine, given in Table 1, simulated that of the brine found at the East Mesa Test Facility. A deposit of scale developed downstream from the cement coupons for a distance of one meter. Adjustment of the brine circulation rate had little effect upon the scaling; thus, the system required cleaning every three months to insure proper flow of fluid through the system.

Other than the chronic scale problem, the D-BETA generally performed well during the testing program. No problems were encountered with the oven or pumping system. The ball check valves were cleaned twice but were never replaced, and the pressure relief valve was tightened and reset once. The coupling between the motor and pump was replaced once. To help remove solids suspended in the brine, filters were placed in the line. Both one and five micrometer filters operated satisfactorily.

If this apparatus is duplicated in the future, the scaling problem may be prevented by utilizing larger tubing and installing elbows instead of bends thus allowing easier inspection and cleaning. Valves and fittings located inside the oven chamber occasionally developed leaks during the latter stages of the test programs. In most cases the leaks sealed themselves due to deposition of evaporated salts, but some had to be stopped by tightening connections.

Sixteen systems were chosen for long term evaluation in the D-BETA. Performance of these systems in terms of compressive strength, water permeability, and erosion is given in Table 8. Initial composition of the slurries is given in Table 3. Many of these were also sent to the Niland and East Mesa Testing Facilities and will be discussed later in this report.

Two general effects of exposure of cement to a circulating geothermal brine were immediately apparent in the D-BETA program. Most systems, especially the lightweight ones, were subject to accelerated deterioration. Also, the carbonate present in the brine appeared to convert the cementitious calcium silicate hydrates to calcium carbonate and silica. The carbonate reaction was most rapid with lightweight systems due to their higher permeability allowing increased brine penetration.

The carbonate degradation most commonly manifested itself in the formation of a scale over the surface of the cement specimen that could easily be scratched away by a fingernail. Figure 9 is a photograph of a typical example. The depth of the scale indicated the degree of penetration of the brine into the cement. The rate of penetration of the normal weight silica stabilized Portland systems was as low as 0.05 in/yr, while some of the lightweight cements deteriorated completely (0.5 in. penetration within 15 months).

X-ray diffraction results revealed little concerning the fate of the calcium silicate hydrates other than their susceptibility to replacement

by calcite and silica when contacted by acidic carbonate brine. Regardless of original slurry composition, calcite was the major detected phase in all of the tests with quartz varying from major to trace amounts. Iron compounds such as magnetite and marcasite were often detected as a trace and anorthite was a trace phase in normal weight Class J and Class B systems. The scales usually consisted of calcite, quartz and magnetite. The deposit in the tubing was chiefly magnetite due to degradation of steel with traces of calcite and marcasite.

To summarize, the D-BETA results indicate that Portland cement compositions with a specific gravity below 1.5 are unsuitable for cementing geothermal formations that contain flowing acidic carbonate brine. Class J systems also behaved much like the Portland systems. Although these results appear unpromising with regard to the use of low density cements for geothermal wells, it is important to remember that, in most situations, only a limited area of the cement sheath would actually be exposed to flowing brine. Several lightweight systems performed well in static tests and would thus perform adequately in most of the annular zone.

GEOHERMAL FIELD TESTING

Testing of cement systems under actual geothermal conditions was performed at two geothermal test sites in Southern California, East Mesa and Niland. The East Mesa Test Site is located in the Imperial Valley, 20 miles east of El Centro. Niland is located further north, along the

southeast shore of the Salton Sea. At both sites hot brine was passed over cement specimens for various time periods.

East Mesa Testing

Five wells are located at the East Mesa Test Site. Temperatures range from 152 to 170°C (306-338 F) and the concentration of dissolved solids in the brines ranges from 1,600 to 26,300 mg/L TDS. A view of the wells at East Mesa is given in Figure 10. Well 8-1 was selected for this evaluation. Fluid temperature was maintained at 150°C (300 F) and 95 psig pressure. The brine analysis is given in Table 2.

Sixteen cement systems were evaluated at East Mesa. All had passed the initial screening evaluation and most had been subjected to the D-BETA simulator. As mentioned in the Phase I section of this report, the test apparatus at East Mesa was very similar to the D-BETA in design. The brine flow rate, however, was much faster at East Mesa, 6.0 L/min. Cement specimens were exposed for periods of 1, 3, 7 and 17 months and evaluated in terms of compressive strength, water permeability, and degree of size reduction. Also, DTA, XRD and SEM were performed on selected samples. Generally, the performance results at East Mesa were very similar to those measured with the D-BETA; however, due to the faster fluid movement, the rate of deterioration or erosion was accelerated. A complete listing of the East Mesa results is found in Table 9. From a compressive strength and water permeability standpoint, only four systems performed satisfactorily throughout the entire 17 months: 3, 6, 10 and 49. Systems 3, 6 and 10 are based upon Class G Portland cement and contain 79% fly ash, 5.4% sodium chloride, and 27% powdered coal,

respectively. System 49 is a Class B slurry with 35% silica sand. All four are normal weight systems. It is interesting to note that, upon 7 months exposure, 11 of the 16 samples were still exhibiting acceptable properties. Elimination of so many systems attests the value of longer term testing when evaluating cements for use under such harsh conditions.

Erosion of the cement specimens was severe for all of the systems. A flow rate of 6.0 L/min is probably on the high side when compared with the average geothermal well situation, so the deterioration may be somewhat unrealistic.

XRD was performed on the 1, 7 and 17 month samples. After 1 month of exposure all the samples showed major amounts of calcite and quartz. Little or no CSH material was detected, implying that the CSH gel had persisted or that the normally encountered crystalline CSH phases were not well established. At seven months the x-ray results were very surprising and not consistent with previous results. Calcite and quartz were mysteriously absent and phases such as unhydrated alite (C_3S), alpha dicalcium silicate hydrate ($\alpha-C_2SH$) and portlandite (CH) predominated. Such phases are normally not associated with acceptable cement performance but, as mentioned earlier, 11 of the 16 samples exhibited excellent strength and low permeability. The 17 month results were once again consistent and logically followed the 1 month results. Calcite and quartz were predominant; however, aragonite, another form of $CaCO_3$, occurred often and small amounts of tobermorite and xonotlite finally appeared.

When contemplating the x-ray results it is important to remember that different specimens were involved in the tests for each time period. In other words, the 1 month samples were not returned to East Mesa for 3 months additional exposure after evaluation in Tulsa. Thus, each set was independent from the others. In the case of the 7 month samples it is possible that the brine did not circulate adequately and the cement specimens dehydrated.

DTA curves were generated from the 7 month East Mesa specimens, and they conflict with the x-ray results. As shown in Figure 11, only three of the curves have the characteristic endotherm for portlandite at 550°C, yet XRD showed this to be a major phase in every system. The fact that DTA can detect portlandite in smaller quantity than x-ray diffraction makes this observation all the more puzzling. At present, no solution to this mystery has appeared.

The 17 month samples were examined by SEM with interesting results. Examination of the micro-structure of the cement specimens can aid in explaining why some cements perform better than others. SEM photographs of the 16 samples are found in Figure 12. At the bottom of each micrograph the magnification factor is shown in the lower left corner. A bar showing a convenient unit of distance appears in the lower center. As a general rule, a significant visual difference is evident between systems of high and low permeability. Visual evaluation of the samples in terms of compressive strength is much more difficult. Some of the high strength samples appeared to be tightly packed with few grain

boundries. EDX analysis was also performed on the samples in an effort to identify phases and note where and how they occur. Phase identification was successful in several cases but, more importantly, amorphous calcium silicate hydrates, not detectable by x-ray diffraction, were located.

System 1 (Photos 1 and 2) was shown by XRD to be composed of calcite, aragonite and quartz. Photo 1 shows what appears to be a crater surrounded by an irregular matrix. EDX analysis showed the matrix to contain calcium and silica, implying an amorphous CSH material. Analysis of the interior at the crater detected only calcium; thus, the area is probably composed of calcite and aragonite. In Photo 2 the dark area is a quartz grain and the matrix is calcium silicate. This specimen was of very low permeability and examination of the micrographs reveals a dense, tightly-packed material.

Photo 3, corresponding to System 2, shows a group of loosely interlocking platy crystals. They were determined by EDX to be calcite. Photo 4, a lower magnification view of System 2, shows a matrix of crystals with varied morphology.

System 3 (Photos 5 and 6), one of the successful Class G formulations, exhibited some interesting structural features. Photo 5, magnified 10,000 times, shows flat circular crystals of calcium silicate. XRD revealed the presence of tobermorite. Perhaps this photograph shows one of the morphologies of the phase. Reduced magnification (Photo 6) shows the calcium silicate crystals to be tightly congregated, explaining the observed high strength and low permeability.

System 5, shown in Photos 7 and 8, was abnormally low in silica when analyzed by EDX. Analysis of the area shown in Photo 7 was performed and only calcium was detected. Looking at a larger area in Photo 8 one sees an unconsolidated matrix.

Photos 9 and 10 show the dense microstructure of System 6, a formulation that performed very well. Photo 9 shows the rather severe topography of the sample. The void that appears at the right center of the photograph is probably due to a dissolved halite crystal. EDX analysis showed the matrix to be principally calcium silicate but, due to the lack of distinguishing features, identification of phases was not attempted.

System 9 (Photo 11) was the poorest performer of the 16 East Mesa samples. Scrutiny of Photo 11 reveals a very loosely consolidated cement with high porosity. EDX analysis of Grain 1 showed calcium, silicon and iron to be present. Calcium and silicon were detected in Grain 2. Only calcium was found in the matrix.

Photo 12 shows the tight, highly consolidated structure of System 10, one of the systems that performed well. Because this cement contained powdered coal, EDX detected a great deal of sulfur in addition to calcium and silicon. Photo 13 is a higher magnification view of System 10. Another good performer, System 17, is shown in Photo 14.

All but one of the remaining systems did not exhibit adequate performance after 17 months at East Mesa. Perusal of the SEM photos for these cements confirms what has been discussed above: cements with low

strength and high permeability appear to be loosely consolidated and porous. Photos 15 and 16 are micrographs of System 22. System 50 is seen in Photo 19, System 52 in Photo 20, System 53 in Photo 21, System 54 in Photo 22, System 61 in Photos 23 and 24, and System 62 in Photos 25 and 26.

System 49, the best cement in the series, is seen in Photos 17 and 18. A relatively low magnification view of the cement (Photo 17) shows a quartz grain with a tightly bonded calcium silicate matrix. Inspection of the matrix, shown in Photo 18, reveals a complex interlocking system of crystals.

In conjunction with the chemical studies program, described later in this report, attempts were made to identify and characterize the commonly encountered calcium silicate hydrates by using the EDX and noting crystal habits. Under carefully controlled conditions this may be feasible. Unfortunately, the East Mesa cements did not produce highly crystalline and abundant CSH phases. As a result, the technique described in the chemical studies section was of only limited use.

Niland Testing

As described in the Phase I section, the design of the Niland Field testing apparatus differed greatly from that at East Mesa or in the D-BETA simulator. The samples were exposed to two 38 day cycles at 170-182°C (340-360 F) and 800 kPa (115 psi). The brine indigenous to Niland is unusually high in dissolved solids. An analysis appears in Table 2.

The samples were exposed to the brine by placing them in a wire cage mounted inside a brine flasher. The specimens were 2 x 2 in. cubes. The wire used to make the cage was very coarse and the mesh was such that the holes were approximately one inch across. Such a cage design was necessary to assure adequate brine contact with the cement cubes. In time, scale formed along the wires and a finer mesh would have plugged. When the basket was removed after each 38 day cycle about 50 percent of the holes were totally filled with scale. A schematic diagram of the system is shown in Figure 13.

The cement specimens at Niland performed much unlike their East Mesa and D-BETA counterparts. Results are given in Table 10. All but one of the systems maintained excellent compressive strength. Strength was not measured on System 56 due to shattering. Permeability could only be measured on five systems because most of the cubes were cracked. As a result, only two systems could be verified as viable geothermal cements: Systems 5 and 61. The behavior of these cements illustrates their susceptibility to thermal shock. Like East Mesa, the conditions experienced at Niland would probably not be seen by most cement in a geothermal well. Thus, the data reported here must be kept in perspective.

X-ray diffraction results for the Niland cements are similar to those of the other dynamic testing procedures. Unlike East Mesa, large amounts of crystalline CSH phases such as xonotlite and tobermorite were detected. Due to the extreme salinity of the Niland brine, halite (NaCl) was commonly encountered. Calcite and quartz were major constituents, further evidence of the ability of carbonaceous brines to attack CSH phases.

DTA curves for the Niland cements appear in Figure 14. The majority of the samples can be seen to have endotherms in the low temperature range of 50-150°C. This is indicative of free and absorbed water on the CSH gel. Such systems are not considered to be of poor quality but are still subject to change in strength and permeability. Sustained curing at temperatures above 150°C usually results in a flat trace below that temperature indicating the transformation of the CSH gel to crystalline CSH. System 10 shows a large exotherm area due to coal oxidation. Most fly ash samples (Systems 3, 54 and 61) had an exotherm due to residual carbon. This exotherm should not cause a problem as long as the well temperature remains lower.

DISCUSSION OF FIELD TESTING RESULTS

Generally, the results of tests conducted at East Mesa and Niland confirmed what had been concluded after analyzing the data from the D-BETA simulator. Portland cement based slurries of normal weight, similar to those already in use at most geothermal areas, appear to be the best systems that current available cementing technology can offer. This fact should be reassuring to operators who have used such slurries in existing wells but, on the other hand, does not offer much encouragement for those who need lightweight slurries. Fortunately, as a result of the chemical studies program, some lightweight systems based upon special modifications of Portland cement appear promising. This research is documented later in the report.

SPECIAL CEMENT SYSTEMS

Although the intent of this research was to evaluate cements based upon commonly encountered oilfield materials, some rather exotic systems were also evaluated as possible geothermal cements. This particular research was very limited in scope but deserves to be mentioned.

Furfuryl Alcohol/Powdered Coal

Acid catalyzed furfuryl alcohol/filler blend systems were selected for evaluation as geothermal binders. Several fillers including powdered coal, graphite, perlite, diatomaceous earth and silica flour may be used with furfuryl alcohol.^{41,42,43} Initial testing showed that the coal system would develop approximately 20,940 kPa (3000 psi) within three days of curing at 300°C. Permeability of this system was about 0.01 md. The light weight and low cost of coal also made this system appear advantageous.

The next step was the determination of pumpability of the furfuryl alcohol/coal system. Problems were encountered because the rubber diaphragms used in high pressure and temperature consistometers were not stable in contact with furfuryl alcohol. The instability caused the diaphragm to contact the stirring paddle in the consistometer cup resulting in false viscosity readings.

As shown in Table 11, furfuryl alcohol without a catalyst will not polymerize in less than six hours at 150°C (300 F) and 35,880 kPa (5,200 psi). Three catalysts were evaluated with varied results. Tartaric

acid and malic acid caused a very rapid set accompanied by a violent exotherm. For safety reasons testing was temporarily halted and calorimetry tests were performed to determine the temperatures at which the exothermic reactions take place and the amount of heat liberated. In an acid catalyzed coal filled furfuryl alcohol resin four separate reactions were identified between 50 and 300°C. Powdered coal will catalyze the polymerization of furfuryl alcohol producing at least two reactions. The addition of one part fine coal to one part furfuryl alcohol appears to control heat evolution sufficiently for most applications.

To alleviate the exothermic behavior somewhat, a 50-50 mixture of furfuryl alcohol and partially polymerized furfuryl alcohol was evaluated. The partially polymerized resin is produced by Quaker Oats and identified as Experimental Resin 4607. A 50 percent solution of ZnCl_2 was utilized as the catalyst and, by varying its concentration from 0.2 to 1.0 percent, the thickening time of the slurry fluctuates between about 2 to 6 hours. A significant exotherm is still experienced with this formulation, but it should not be problematic in a field situation.

Two of the furfuryl alcohol/powdered coal systems were evaluated for compressive strength and permeability characteristics. Briefly, this system gives excellent strength and low permeability at high temperatures provided the material is in contact with fluid. When subjected to dry heat severe oxidation occurs resulting in a loss of integrity. After these tests, work was terminated.

Epoxy and Polystyrene Cements

Following the discontinuation of research with the furfuryl alcohol/powdered coal system, further efforts were made to find candidate synthetic polymer cement systems. The search was limited to commonly available network forming polymers.

Economic considerations dictated that the polymers must be capable of being placed with a filler material to increase yield to say nothing of stability in a geothermal environment. Practicality being paramount, the more economical network polymers such as epoxides, urethanes, and crosslinked polystyrenes were investigated. Emphasis was placed on in situ polymerizable materials in order to decrease pumping pressures against fragile geothermal formations. The possibility of using low viscosity partially polymerized materials was also considered in order to lessen the exotherms during set.

Epoxy/hardener systems with silica fillers are currently used in the oil industry for controlling sand migration into a producing wellbore. Although these epoxide systems are designed to be highly permeable to fluids, the permeability can be substantially reduced by simple modification of materials and mix ratio. Epoxy resins are known to be susceptible to thermal shrinking at high temperatures ($\sim 225^{\circ}\text{C}$) even at high filler levels.⁴⁴ Curing the resins at high temperatures alleviates the problem somewhat, but the strength of the set resins is lower; as a result, the resins are subject to creep (plastic deformation) beginning at 200°C . Creep is undesirable as it leads to polymer movement away from the filler and loss of tensile and compressive strength. Creep

will generally take place at temperatures approaching a polymer's characteristic glass transition temperature (T_g). Although creep may be appreciable below T_g , this temperature is a rough guide to the upper temperature limit of a polymer's mechanical utility. The glass transition temperatures of selected polymers appear in Table 12.^{44,45,46} Formulations of epoxide which are less susceptible to creep are very brittle and contain a large amount of hardener. Thus, epoxy resins were deemed unsuitable at the high temperatures encountered in a geothermal well.

A study of the literature concerning possible crosslinked polystyrene or polyurethane systems was undertaken. Polystyrene systems were found to have undesirable placement properties, especially in systems with fillers. In addition, the low glass transition temperature leads to creep in the set polymer. Polystyrene degrades thermally by depolymerization beginning at 250°C and would not be desirable for use at high static bottom hole temperatures.

Polyurethane systems suffer from much the same drawbacks as polystyrenes. However, the polymerization reaction is easier to retard. The use of fillers with polyurethanes is uncommon due to the extensive use of polyurethanes in lightweight applications, especially foams. Thermal degradation of polyurethanes can be prevented up to 225°C ; however, use of special techniques is required above 150°C .

In conclusion, no commonly available network forming polymers were found which would provide the desired performance under geothermal well conditions; therefore, testing was not indicated.

Ultra-Lightweight Glass Bubble Cement

Portland cement slurries with densities in the 0.96 to 1.20 kg/L (8-10 lb/gal) range are possible with the utilization of lightweight glass bubbles, or microballoons, having a specific gravity of approximately 0.35. Such slurries have been shown to have acceptable properties under normal oilfield conditions.⁴⁷ Glass bubble cements must be prepared and utilized with care. Depending upon the grade of bubbles, the lightweight slurries can retain their designed properties only when the hydrostatic head does not exceed 500 to 2000 psi. The cost of these special systems is also considerably higher than conventional cements.

Because slurries of such low density are desired in geothermal applications, an evaluation of their suitability was conducted. Twenty-one candidate systems, described in Table 13, were subjected to compressive strength and permeability testing following exposure to simulated geothermal conditions. Compressive strength and water permeability results are listed in Table 14.

Two grades of commercially available glass bubbles were used in this evaluation, Grade 1 and Grade 2, a stronger and more expensive bubble with a greater collapse pressure. The slurry densities of the glass bubble systems varied from 1.07 to 1.57 kg/L (8.95 to 13.1 lb/gal). Various amounts of silica flour were also added to evaluate the effect of glass bubbles on the strength and permeability of the cement. Results show that when glass bubble cements are subjected to geothermal temperatures, at least 20 percent silica must be added to prevent

strength retrogression. Otherwise, the glass bubbles themselves react with the cement resulting in disintegration of the bubbles and a highly permeable cement.

As a group, the glass bubble cements performed much better than similar weight conventional systems. Under extremely critical conditions, where ultra lightweight slurries are essential, the glass bubble systems would be advantageous. In less demanding situations, the operator would need to decide whether the substantially higher cost of these systems would be justified.

SELECTION OF RECOMMENDED GEOTHERMAL CEMENTS

According to terms specified in the research contract, Dowell and other contractors were to submit suitable geothermal cement systems to the National Bureau of Standards (NBS) for testing and verification. As Dowell's contract term approached termination a final review of test results was performed and six basic systems were selected. They are listed below.

1. Class G + 35% silica flour + 54% water
2. Class B + 35% silica flour + 54% water
3. Class J + 44% water
4. Class G + 35% silica flour + 2% bentonite + 8.5% perlite +
116% H₂O
5. Class G + 35% silica flour + 10% diatomaceous earth + 91%
H₂O
6. Class G + 100% silica flour + 2% sodium silicate extender +
136% H₂O

The first three slurries (Systems 2, 50 and 16) are of normal weight. The remaining systems (Nos. 4, 9, 13) are lightweight.

The three lightweight slurries behaved rather erratically in the circulating brine tests but performed well in static tests. Because only a limited amount of cement would actually be exposed to circulation, the lightweight systems listed above should give adequate performance. As mentioned in the Phase I section, the slurry containing bentonite and perlite is already a commonly utilized system.

The six systems are compatible with common retarders and fluid loss additives. Table 15 shows typical performance of eight systems based upon the six basic formulations. In two instances fluid loss is excessive; however, adjustment of the concentration of fluid loss additive would probably remedy the situation. Samples of the six basic systems were sent to NBS before December 31, 1979.

As a final step in verifying the suitability of the six proposed geothermal cements, compatibility with drilling muds was evaluated. Mud removal is essential in the cementing process. If 100 percent of the mud is not replaced by the cement, a potential exists for the formation of a flow channel that could result in casing corrosion due to exposure to formation fluids. Other consequences include production of unwanted zones and ineffective stimulation treatments.

Incompatibility can vary from the formation of a thickened interface between the mud and cement to a severely clabbered mass that could

result in bridging off the annulus. The thickened interface that can form upon cement-mud contact is extended by the thinner cement "fingering through" the original interface and contacting additional drilling fluid. As a result, gelled mud is left behind along pipe and formation surfaces. Because gelled mud does not develop strength, support of casing and isolation of producing zones can be severely compromised.

A higher degree of incompatibility can result in increased pumping pressure due to the high viscosity of the thickened cement-mud mixture. Such pressure increases could be devastating in a geothermal well completion. Fracturing of weak formations and lost circulation difficulties are possible consequences.

Due to the critical nature of geothermal wells with respect to treating pressures, zonal isolation and bonding, the slurries selected for submission to NBS were evaluated as to their compatibility with a commonly used drilling fluid. All the slurries behaved in much the same manner; thus, one typical slurry will be discussed, Class G + 8.5% perlite + 3.0% bentonite + 35% silica flour + 116% H₂O. The density of this slurry is 13 lb/gal. The drilling mud weighed 9 lb/gal and had the following composition: 21 lb sepiolite, 1 lb liquid dispersant, and 2 lb sodium polyacrylate added to one barrel (44 gal) of water.

Compatibility can be demonstrated by mixing various ratios of two fluids in a bottle and determining the rheological properties of the mixture with a viscometer, in this case the Fann 35 V-G Meter. The results of the "shake bottle" tests for the cement-mud mixtures are plotted in

Figure 15. The apparent viscosity at a shear rate of 512 sec^{-1} corresponds to the Fann V-G Meter reading at 300 RPM. The drilling mud-cement mixtures gave somewhat erratic apparent viscosities due to perlite particles interfering with the rotor and bob on the viscometer. All mud-cement mixtures were not pourable upon initial mixing; however, additional shearing broke the gel. Incompatibility such as this would not cause pumping difficulties in a field situation, but mud removal could be incomplete.

Frequently the use of spacers and washes can prevent pressure increases and poor mud removal due to mud-cement incompatibility. Spacers and washes are fluids which are pumped between the mud and cement to prevent contact and facilitate proper mud removal. Of course, these fluids are compatible with both mud and cement. Spacers are thick fluids that act as a piston to remove mud from the annulus. Washes are thin fluids that remove mud by turbulent action, thinning the mud and scrubbing formation surfaces.

Results shown in Figure 15 demonstrate that the incompatibility observed for mud-cement mixtures can be eliminated by using a spacer system that is compatible with both the drilling mud and cement slurry. The spacer used in this evaluation was a gelled water system containing surfactants and fluid loss additives. In Phase I none of the operators utilized intermediate fluids between mud and cement. In light of the study described above, it may be advantageous to use spacers in geothermal well completions.

CHEMICAL STUDIES

The chemical studies program was divided into two parts. First, as a supplement to the screening and dynamic testing programs, chemical analysis of test cements was performed using XRD, DTA and SEM. This area has been covered in sufficient detail in previous sections. The second portion concerned the performance of basic research. A more thorough and precise knowledge of the chemical behavior of calcium silicate hydrates at elevated temperatures, to say nothing of geothermal brine exposure, has been needed for a long time. Thus, a separate research program was performed concurrently with the screening and dynamic testing with two primary goals: (1) finding a chemical explanation for the somewhat unpredictable behavior of high temperature cements, and (2) evaluating high temperature calcium silicate phases, other than xonotlite, as possible geothermal cements.

Effect of Silica Particle Size on Performance of Geothermal Cements

As reported earlier, many of the cement systems entered into the screening program failed to meet minimum strength and permeability requirements and were dropped from further testing. During this phase of the screening program it was noted that the behavior of silica stabilized Portland cements cured in heavy geothermal brines (25 percent dissolved solids) was dramatically affected by the particle size of the silica originally added to the cement. Portland cements containing fine silica sand (100 μ m) consistently failed both the strength and permeability tests, while those containing silica flour (45 μ m) performed

satisfactorily. In an effort to explain this observation, more extensive research was performed.

The particle size and calculated surface areas of the cements and silicas used in this investigation are given in Table 16. The mixing closely followed the API procedure for preparing compressive strength cubes. Appropriate amounts of effective retarders were added. Rather than the standard two-inch cubes, one-inch diameter cylinders 1.25 inches long were prepared. The samples were cured under 20,700 kPa (3,000 psi) pressure at 150°C (300 F) for 24 hours. The cylinders were shaped to one-inch prior to any initial measurements. The weight, size, and permeability of all the cylinders were then determined. Water permeability was determined using a modified Ruska permeameter.

The samples were cured in small autoclaves containing brine. Brines corresponding to those found at East Mesa (3 percent TDS) and Niland (25 percent TDS) were used in these tests. Oxygen was removed from the mix water, and the brines were stored in capped glass bottles under nitrogen to prevent excess oxidation of the ferrous iron. A 14 percent brine solution was prepared by mixing equal volumes of the 3 and 24 percent brines. Duplicate coupon cylinders of each test material were placed in an autoclave with steel washers as spacers to isolate systems. After an autoclave was filled with coupons, the remaining space was half filled with brine and the autoclave closed and numbered. The autoclaves were placed in ovens and brought to the appropriate temperature in eight hours. Curing times varied from seven days to one month. Fifty-eight cement formulations were exposed to water and 24 percent brine at 150, 232 and 325°C (302, 450 and 608 F).

The solubilities of silica in the various brines were determined in a Baroid high-temperature, mud-aging cell. The cell was rotated at 35 RPM at 260°C (500 F) in a roller oven. Approximately one hour was required for the samples to reach oven temperature. Samples of brine (50-60 ml) were removed through the pressurizing and drain valve after 1 hr, 2.5 hrs, and 5 hrs heating periods. A back-pressure receiver was used to collect the sample. The silica in solution was determined by plasma emission spectroscopy.

The effect of brine solutions on Portland cements at high temperatures was first studied on lightweight systems. Typical systems are shown in Table 17 by fresh water mixes 1A and 1B containing silica sand and silica flour. These were tested in water and brines containing 3 to 24 percent dissolved solids. Compressive strengths are shown in Figure 16; the mix stabilized with silica flour, given in Table 17, maintained most of its strength in dense brine while the mix stabilized with silica sand, given in Table 17, deteriorated considerably in the brine solution. The reported strengths were measured following 28 days of curing. Very little change in strength was noted after seven days.

The effect of addition of up to 37 percent salt to the mix water is shown in Figure 17. The cement with silica flour was not seriously affected by any salt addition as shown by relatively uniform strength and permeability. The silica sand caused serious deterioration. Note that the permeability data in Figure 17 are plotted on a logarithmic scale, and that the permeabilities of the salt saturated cements

containing silica sand are approximately 100 times greater than those of cements containing silica flour.

As shown in Figure 18, increasing the amount of silica sand in the Portland cement improves the performance, but at least 100 percent was required to approach the stability provided by 35 percent silica flour. However, the additional sand is detrimental in producing a lightweight cement since it increases density considerably. Although the strength at 150°C(300 F) is slightly low, the permeability is very good.

Tests were conducted on normal weight cement with 40 percent additions by weight of cement of various narrow fraction silicas. The six fractions shown in Figures 19 and 20 ranged from approximately 175 μm to a water-flotation cut averaging about 3 μm . Figure 19 gives strength and permeability results obtained with Class B, Class G and Class H Portland cements. Figure 20 depicts the results obtained with the Class G cement in heavy brine at 150, 232, and 325°C (300, 450, and 617 F) and by dry heat at 325°C. In all these systems using 40 percent silica, severe deterioration occurred when silica coarser than 45 μm was used. The fractions finer than 45 μm tended to give approximately the same trend of results except for that averaging 3 μm . The 3 μm silica was tested with Class G cement only. It was very difficult to mix the cement with the 3 μm silica compared to the other fractions. The slurry was considerably thicker and contained entrained air. Even after attempts to remove the air, the set cement was 8 percent lighter than the other systems. The 8 percent air probably accounts for the increased permeability and the reduced strength.

Figure 19 shows that the cements deteriorated similarly, although the coarse Class H cement had the least deterioration with the coarser silica. Not shown in Figure 19 are results on a coarse-grind Type I cement (modified Class A). It had a grind and strength loss similar to that of the Class H. Tests on a fine-grind Type I slag cement, slightly finer than Class G, gave results similar to those of Class G. These results demonstrate that the fineness of commercially available cement is not nearly as important as the fineness of the silica. Figure 20 shows that the deterioration of cement systems stabilized by coarse silica is far more serious at 325°C (617 F) than at 150°C (302 F).

Figure 21 shows what happens to a lightweight Class G cement system for the conditions depicted in Figure 20. The two results are similar although strengths of the lightweight systems are about half that of the normal cements, and the strength behavior is less regular with temperature. Other lightweight cement systems containing bentonite, diatomaceous earth or silica gel as the extender gave similar results.

The results of dry heat at 325°C on normal and lightweight cements are shown by the dotted lines (D) in Figures 20 and 21. Normal weight cement apparently deteriorates little under dry conditions regardless of the particle size of the cement. Lightweight cement will deteriorate under dry heat if it contains a coarse sand. Note that these coupons were not exposed to salt brines.

Figure 22 indicates at what temperatures a saturated salt cement will retain strength if stabilized by silica flour or by silica sand. At

150°C (302 F) 35 to 40 per cent of either form of silica will stabilize a normal weight or lightweight Portland cement system. At 232 to 325°C (450 to 617 F) only the silica flour should be used. Tests have not been conducted to define the point between 150 and 232°C where the deterioration starts. The reasons for believing there is no sharp break will be discussed in later paragraphs of this section of the report.

The reaction products of Class G Portland cement systems containing various sizes of silica were examined by XRD after exposure for 28 days at 325°C (617 F). The compounds found by x-ray are listed in Table 18 while strengths and permeabilities are shown in Figures 19 and 20. The low strength and highly permeable samples prepared with the coarser silica were found to be high in kilchoanite (C_3S_2H), a tricalcium disilicate hydrate compound. Kilchoanite is rare in nature and seldom found in cements exposed to steam or fresh water at elevated temperatures. The Portland cements containing the finer silica were found to be high in xonotlite (C_6S_6H) under present testing conditions. Both products are known to be alteration products of tobermorite ($C_5S_6H_5$), the usual predominant phase at temperatures below 150°C (300 F). Figure 23 graphically illustrates the results of work performed to determine the solution rates of silica in 3 and 35 percent sodium chloride solutions at 260°C (500 F). Under slow agitation, there is approximately a three-fold decrease in silica solubility from 3 to 35 percent sodium chloride.

It is apparent that the density of the brine and the particle size of the silica are factors which influence the formation of kilchoanite or

xonotlite. The exposed surface area of the silica decreases markedly with increased particle size, which results in a lower concentration of silica in solution. As a result, the silica deficient kilchoanite tends to be favored. There is evidence that kilchoanite is more stable in a heavy brine than in a light brine. Alpha dicalcium silicate hydrate is normally the observed degradation product in steam or hot light brines. These observations indicate that the chemistry of calcium silicate hydrates becomes much more complex when the reactions products are formed under geothermal conditions.

The observed degradation of the cements in high temperature brines cannot be attributed to changes in the stability of the crystalline xonotlite, kilchoanite, or tobermorite. Otherwise, such behavior would have occurred throughout the entire range of silica particle sizes. Likewise, the total solubilities of calcium hydroxide and silica in the brines are not determining factors, because all grades of silica would be affected, and because the solution reactions that occur between calcium and silica are essentially completed before a saturation level is reached. The saturation solubility of calcium hydroxide decreases with temperature while that of silica increases. At 250 to 300°C (482 to 572 F), silica is several times more soluble than calcium hydroxide.

The observations discussed above lead to the hypothesis that the phenomena associated with calcium silicates under geothermal conditions are due to changes in the kinetics of the solution reactions. The rate at which silica enters solution could definitely be affected by both the silica particle size and the brine density. If a fine grind of silica

is employed, silica will enter solution more quickly due to the larger surface area. The brine density affects solution rate of silica in a converse manner. Due to increased ionic strength in high density brines, the entrance of silica into the solution is inhibited.

Only limited published information concerning the rate of solution of silica is currently available. Work performed by the U.S. Geological Survey has indicated an abrupt decrease in rate of silica solution between 2N (10 percent) and 4N (20 percent) sodium chloride solutions.⁴⁸ The results concerning silica solution rate relate directly to the earlier observation that at least a 2.5 fold increase in the relatively coarse 70-200 mesh silica was required to produce satisfactory cements at 232 to 325°C (450 to 617 F). The 70-200 mesh silica was also found to dissolve only 20 to 25 percent as fast as silica flour during the first few hours after initial exposure (Figure 23.)

From a practical viewpoint, the results of this research have indicated that 45 μ m silica flour appears to be the near optimum material for stabilizing Portland cements for geothermal applications. The rate of silica solution is a critical factor in determining whether a cement will be stable under these severe conditions. Silica flour is the correct balance between two opposing relationships concerning silica solution rate: 1) the smaller the silica particle size, the faster the solution rate; and 2) the denser the brine, the slower the rate.

High Temperature Cement Phases

Cement phases with a C/S ratio less-than or equal-to one generally have

higher strengths and lower permeabilities. At temperatures above approximately 150°C (302 F) tobermorite cement can convert to xonotlite (C_6S_6H), gyrolite (C_2S_3H approx), truscottite ($C_7S_{12}H_3$), pectolite (NC_4S_6H) or scawtite ($C_7S_6\overline{CH}_2$) depending upon the amount of silica present, other materials available for reaction and environmental exposure. These properties will be discussed separately.

Tobermorite cements heated to above 150°C (302 F) should eventually convert to xonotlite and gyrolite. In actual practice, Portland cement slurries stabilized with about 35 percent silica will almost exclusively convert to xonotlite with only a trace of gyrolite. Xonotlite has been found to persist up to at least 315°C (600 F); according to literature, it can persist to above 370°C (700 F).⁶ As a binder xonotlite is generally about 20 to 25 percent lower in strength than tobermorite. Its compressive strength exceeds 35 MPa (5,000 psi) for neat cements (1.92 g/cm³ or 16 lb/gal), and is adequate except in highly extended light weight systems. The strength and permeability of xonotlite systems extended with large quantities of water is shown in Figure 24. The permeability of xonotlite cements is usually about 4 to 5 times that of tobermorite. This may lead to fluid penetration of light weight systems in critical areas. Penetration by well fluids may cause phase changes and deterioration as shown in Figure 25. Slurry compositions are listed in Table 19. Acidic carbonate fluids will convert the cement to calcium carbonate and silica.⁴⁹ Hot brine exposure can also cause strength loss even though xonotlite persists.¹⁰ This may be due to recrystallization which produces larger grains and results in less bonding area.

Truscottite is weaker but less permeable than xonotlite. The suggested formula for truscottite is $C_7S_{12}H_3$, but other formulae have been proposed. Truscottite has a higher silica content than xonotlite but both require approximately equal amounts of silica and Portland cement in the initial slurry. The silica must be in an active, highly soluble form such as fine silica ($45\mu m$ or less), and in a slight to highly basic environment at temperatures ranging from 215 to 315°C (420 to 600 F).

With the addition of more active forms of silica, such as amorphous or hydrous silica, almost pure truscottite can be formed at temperatures as low as 150°C (302 F). Figure 26 shows the performance of several cement systems in which truscottite was the predominant phase. Table 19 gives the exact slurry compositions. Although the strength of truscottite is slightly lower than xonotlite in normal and intermediate weight formulations, its strength is still acceptable. Its permeability is approximately one fifth to one-tenth that of xonotlite. In a lightweight truscottite mix, only the hydrous silica formulation proved to be a consistently good cement. Other silicas behaved inconsistently and often produced xonotlite with low strength and high permeability. Such behavior implies that truscottite may be metastable to the more commonly encountered xonotlite. The recrystallization of truscottite to xonotlite and quartz was observed by Taylor and Luke⁵⁰ at 275°C (527 F) in an open system where silica could escape from the cement. In a closed system, truscottite is very stable but probably would be difficult to produce and maintain in a geothermal environment.⁵¹

Pectolite is a sodium substituted calcium silicate ($\text{NC}_4\text{S}_6\text{H}$) which is frequently associated with zeolites and highly basic basalt deposits. Nelson and Kalousek⁵² frequently produced this phase by exposing tobermorite samples to sodium salt solutions (other than sodium chloride) at high temperatures. They reported pectolite to be strong and very stable once formed. In this study the formation of pectolite from Portland cement was somewhat unpredictable. The addition of extra silica and sodium hydroxide often produced truscottite or a combination of xonotlite or truscottite with pectolite. Formation of pectolite is accelerated by adding a slightly soluble sodium silicate such as ($\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$ to the slurry).

Pectolite is formed slowly at 150°C (302°F) and more rapidly at higher temperatures. Once formed, it appears to be very stable from 150°C to above 315° (600°F). The performance of cements containing pectolite is illustrated in Figure 27. Of the phases tested in this evaluation, the only lightweight cements that consistently resisted deterioration under geothermal conditions with circulating brine were those containing pectolite. Cement formulations containing pectolite have about the same strength as xonotlite but have permeabilities as high as or higher than xonotlite. In some light weight formulations the permeability was slightly above the recommended limit 0.1 md. Combinations of pectolite and truscottite usually have permeabilities slightly lower than xonotlite.

Scawtite ($\text{C}_7\text{S}_6\overline{\text{CH}_2}$) is often encountered at high temperatures in calcium silicate cement formulations that contain carbonate, or in

systems that contact brines containing carbonate. Trace amounts of scawtite are usually found in high temperature oil well cements and geothermal cements, but only rarely as the predominant phase. Scawtite is reported to be stable between 140° and 300°C (284 and 572 F),⁵³ and can be thought of as xonotlite with 5.3 percent carbon dioxide replacing a portion of the silica. It is prepared in the laboratory at temperatures between 215° and 315°C (420 to 600 F) by adding small amounts (less than 10 percent) of sodium carbonate, sodium bicarbonate, or finely calcium carbonate to Portland cements containing 36 percent silica.

Scawtite can enhance the performance of cement when present in trace amounts, but will exhibit poor performance when it is the main constituent. Results of field and laboratory tests of cements containing various amounts of scawtite are shown in Figure 28. It is believed that water solutions of carbonic acid (carbon dioxide) enter pores producing a more competent cement.

Berger⁵⁴ reports that carbonation of calcium silicate structures results in a stabilized silica structure that retains the morphology of the original silicate. However, when scawtite becomes the predominant phase, it may be a weak material or have a high degree of crystallinity leading to brittleness.

This study has resulted in the characterization of high temperature cement phases. It has been noted that each phase possesses certain unique properties. The ultimate goal of this research was to find a material as easy to produce as xonotlite, as impermeable to fluids as truscottite

and as stable to severe downhole environments as pectolite. Although none of the phases discussed here meet the above criteria by themselves, combinations may prove to be suitable. For example, under controlled laboratory conditions, calcium silicate cements containing combinations of pectolite and truscottite were prepared, resulting in a compromise of their properties. Data for these systems appear in Figure 29. Slurry compositions are given in Table 3. The permeabilities of these cements were lower than those of pectolite or xonotlite, and their stability was greater than either truscottite or xonotlite. Accordingly, the permeabilities were higher than truscottite and stabilities were worse than that observed with pectolite. Whether such combinations can predictably be produced under various field conditions has yet to be investigated.

We consider the highly silicious ($C/S < 1$) calcium silicate hydrates to be promising as high temperature binders, but there is a need for further research. Although this study determined that powdered hydrous silica added to Portland slurries produces an excellent low permeability truscottite cement at elevated temperatures, other researchers have found that hydrous silica aggregate added to concrete produces unsound autoclaved concrete products. Also, the use of fly ash as a source of silica has led to production of reyerite, an undesirable modification of truscottite.¹⁷ It is not always clear whether the difference in observed results is due to differences in materials, particle size, or curing conditions. In any event, caution should be exercised when adding silica in a form other than quartz to Portland cements for high temperature applications.

The tendency of corrosive downhole fluids to penetrate lightweight cements resulting in increased permeability and decreased strength, as shown in Figure 25, is of great concern. These physical changes are frequently accompanied by changes in the cement composition. Normal or heavy weight cements are not easily penetrated by fluids and their changes in chemical composition or strength are not as dramatic. Calcium silicate cements exhibit little or no change if cured in a dry environment. Consequently, any cements which are uphole and are dried by heated fluids inside the casing should be stable.

Investigation of Use of SEM In Cement Research

Many hours of testing are involved in the evaluation of cement systems. The most frequent tests include measurements of thickening time, compressive strength and permeability. XRD analysis is also performed to identify crystalline minerals within the cement. In this research with geothermal cements, simply knowing which crystalline phases were present was not fully satisfactory when trying to make conclusions concerning the phases' effects upon compressive strength and permeability. The analyst needs to know where the phases are located within the sample.

Cement phase location is important because it may be the key to understanding factors that control physical properties. As reported earlier, certain silicate phases seem to be associated with high compressive strength or low permeability. Visual observation and identification of these phases by SEM could help in finding an explanation.

This study employed the AMR 1000A Scanning Electron Microscope in combination with a Tracor Northern TN 2000 Energy Dispersive X-Ray Analyzer. Explanation of the principles by which these instruments operate is beyond the scope of this report.^{55,56,57} The SEM was used to observe the morphology of the cement and hopefully visually identify crystals of the various calcium silicate hydrates. EDX was used to obtain an elemental analysis of the area of observation. By analyzing for Ca and Si, C/S ratios could be determined to verify that a particular calcium silicate phase was under observation. Figure 30 shows a typical output from the EDX.

The C/S ratio acts as a fingerprint in phase identification because each phase has a distinct amount of calcium and silicon as dictated by its chemical formula and crystal structure. C/S ratios for phases of interest are listed below.

<u>Phase</u>	<u>C/S Ratio</u>
C-S-H Gel	1.3 to 2.4
Tobermorite	0.83
Xonotlite	1.0
Truscottite	0.6
Pectolite	0.66

When conducting a quantitative study using the SEM/EDX the following scope settings must be kept strictly constant for reproducibility.

kV (Power)

Spot Size

Thickness of Coatings

Beam Current

Working Distance

Take Off Angle

Flat Surface

Other factors need to be dealt with in quantitative work. They include calculating absorption factors, atomic number, and fluorescence corrections. One of the positive benefits of the ratio method is that it enables the exclusion of calculating absorption factors and matrix corrections, giving the chemist some variance in microscope setting (excluding working distance). During individual EDX tests the intensities of calcium and silicon peaks do not correspond to true amounts. This variation is due to many factors that equally affect the calcium and silicon peak heights. By taking the ratio of calcium to silicon, the factors will cancel each other out leaving a value representing a ratio of C/S. This representative ratio means nothing until a calibration curve is constructed from standards of known C/S ratios whose composition best approximates the composition of the cement samples to be studied. The standards are placed in the SEM and an EDX analysis is run for a 30 second interval at the optimum working distance. The C/S peak ratio is determined and plotted on the calibration curve. The X-axis represents the standards' C/S ratios, and the Y-axis represents the ratios of the standards calculated by peak height. The coordinates produce a straight line. After a C/S ratio is calculated by peak height it is compared to the curve to determine the actual C/S ratio in the sample.

In all semi-quantitative work, the working distance setting on the SEM should be kept constant. Working distance controls the amount of energy reaching the EDX detector. A low working distance positions the sample very close to the detector; consequently, the detector will see too much energy from the sample and the EDX will be unable to record all the information. At a large working distance, the sample and EDX detector are too far apart to record the information.

This feasibility study has pointed out some problems, but the overall results are encouraging. Preparation of the standards seems to be the critical problem and demands the most attention. In the process of data acquisition the reliability of the data is only as good as the quality of the standards used. Care must be exercised in selecting pure refined materials of calcium and silicon. This study used calcium carbonate and powdered silicic acid. Pure reagent grade materials are needed to assure that no error is introduced by foreign substances.

The selection of silicic acid was made due to the fine powder (100 mesh) and the purity which the compound assumed. It was believed that heating silicic acid at 900°C for 16 hours would remove the H₂O, leaving pure silica behind. Results showed the dried material to be 73.1 percent SiO₂, the remainder being H₂O. This error was not discovered until after the standards were prepared. Realizing the error, appropriate changes were made. For example, if the standard supposedly contained a 1.0 C/S ratio, it actually had a 1.37 C/S ratio.

It is important that materials being mixed together have the same particle size. Failure to control particle size introduces error because smaller particles have greater surface area and will emit a disproportionate amount of X-ray radiation, thus influencing corresponding peak height. Both materials used had a statistical variance in particle size. To overcome this obstacle, several EDX runs were performed to obtain an average. Figure 31 shows the results. It can be seen from the graph that a wide range of ratios for the same standard were measured. Such a large variance in readings was rather disturbing, but after calculating the average C/S ratio for each standard, a straight calibration line could be drawn. To test its credibility, standards of C_3S and C_2S were tested. The results fell very close to the standard curve developed by the calcium carbonate-quartz standards.

One cement sample appeared to be totally composed of truscottite when analyzed by X-ray diffraction. Qualitative SEM examination of this sample revealed a unique crystal structure shown in Figure 32. With successive EDX runs on these structures, an average peak ratio of 0.715 was determined. The corresponding measured ratio calculated from the calibration curve would be just under 0.6. This ratio agrees very closely with the published ratio for truscottite. Such results attest the accuracy of the calibration curve. Because of limited time, no other phase identifications were made by this method.

Figure 33 is a lower magnification view of the same cement containing truscottite. Recalling that truscottite cements usually are of low permeability, this photograph may help to explain. The truscottite

crystals seem to occur in the pore spaces of the cement. They could presumably block invading fluids from entering the interior.

Although this study was of very limited scope, it effectively illustrates the potential usefulness of SEM and EDX in cement research. Identification of additional phases by this technique is definitely indicated for future research.

CONCLUSION

This report, along with those from the other contractors in this DOE sponsored study, represents the most comprehensive and thorough examination of the geothermal cementing problem undertaken thus far. Many discoveries were made during these three years of research and the more significant ones are briefly discussed in this concluding section.

Circulating Temperatures

Contrary to what had originally been presumed, the circulating temperature of geothermal wells is seldom above 116°C (240 F). As a result, set cement can be exposed to severe thermal shock upon production of the well. Also, phase transitions and recrystallizations probably occur within the cement, potentially resulting in degradation.

Cementing Costs

Most geothermal cementing costs lie between \$20,000 and \$50,000. Operators are willing to accept no more than a 10 percent cost increase for an improved cement. Except for the most critical wells, such a cost limitation effectively eliminates the more exotic cement systems from serious consideration.

Chemistry of Geothermal Fluids

The character of geothermal fluids varies from essentially fresh waters

to extremely corrosive brines. Also, non-condensable gases such as CO_2 and H_2S are frequently present.

Performance of Candidate Cement Systems

After the processes of screening, dynamic and field testing, etc., normal weight Portland cement systems emerged as the best performers. Systems based on Class J cement also performed adequately. Some lightweight Portland slurries were adequate in static tests but tended to disintegrate when exposed to circulating fluids. Nevertheless, three lightweightes were selected for submission to the National Bureau of Standards in the belief that, because only a small amount of cement would be exposed to flowing brine, the cements should perform satisfactorily.

Cement/Drilling Mud Incompatibility

A slight degree of incompatibility was noted when the NBS destined slurries were tested with a common drilling fluid. The thickening that occurs upon contact could conceivably result in increased pumping pressure and damage to fragile formations. As a preventive measure, use of spacer fluids or washes may be indicated.

Attack of Cements By Geothermal Brines

Geothermal brines that contain significant amounts of carbonate or sulfate evidently are able to attack calcium silicate hydrates. Exposed cement specimens were found to contain high amounts of calcite, anhydrite

and free quartz. Often the degradation manifested itself in the form of a scale on the outer surface of the cement that could be easily scratched away.

Polymer Cement Systems

Some polymers were investigated briefly as potential geothermal cements. A system based upon a mixture of furfuryl alcohol and powdered coal showed early promise; however, more extensive testing revealed some rather disturbing properties, notably a tendency to undergo violently exothermic polymerizations. Epoxy, polystyrene and polyurethane were briefly studied but found to be practically and economically unsuitable.

Glass Bubble Cement

Portland cements containing microballoons made of glass have been shown to be excellent lightweight systems and seemed promising as the ideal lightweight cement desired by geothermal operators. Testing shows that these cements perform better than other systems in the low density range, but the improvement may not warrant the significant cost increase. Also, the glass bubbles have a tendency to react with the cement at high temperatures resulting in high porosity.

Silica Stabilized Portland Cement in Geothermal Wells

When cement is to contact concentrated geothermal brines the use of silica flour instead of silica sand is necessary. Highly saline brines

depress the solution rate of silica and inhibit the entrance of silica into important reactions. The use of silica flour, by virtue of its high surface area, allows the formation of desired C-S-H phases.

High Temperature C-S-H Phases

Xonotlite is normally produced above 150°C by Portland cement containing an additional 35 percent fine silica. Lightweight formulations with specific gravities of 1.5 (12.5 lb/gal) or less have high permeabilities and are degraded by carbonated formation brines. Truscottite, produced by adding silica to yield a product having a lime-to-silica ratio below 0.7, has lower permeability than xonotlite but shows no improvement in stability. Pectolite, a sodium calcium silicate produced by adding an active sodium source to a truscottite type formulation, is stable to corrosive brines, but is highly permeable. Scawtite, a calcium silicate carbonate hydrate, is produced by exposing xonotlite to carbonates. By itself scawtite is not a good cementing compound; however, in trace amounts it can improve the performance of the binder. A combination of truscottite and pectolite can be produced in the laboratory but may be difficult to produce in the field.

Use of SEM/EDX In Cement Analysis

A feasibility study has revealed strong potential for using the scanning electron microscope along with energy dispersive x-ray analysis to help explain the behavior of cements. Scrutiny of the morphology and microstructure can be related to the physical properties a specimen exhibits. Location of crystals of various C-S-H phases is also possible.

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TABLE 1
COMPOSITION OF SYNTHETIC BRINE USED IN DYNAMIC BRINE
EXPOSURE TESTING APPARATUS (D-BETA)

<u>Species</u>	<u>Concentration (mg/L)</u>
Na	8,100
Ca	1,360
K	1,050
Fe	9
Ba	14
Sr	320
Li	40
B	10
Mg	17
NH ₄ ⁺	41
Cl ⁻	15,850
CO ₂ *	200
SO ₄ ²⁻	43
TDS (calc)	27,050

* CO₂ includes carbonate in all forms

TABLE 2
ANALYSES OF GEOTHERMAL BRINES AT EAST MESA AND NILAND TEST FACILITIES

<u>Species</u>	<u>Concentration (mg/L)</u> <u>East Mesa</u>	<u>Concentration (mg/L)</u> <u>Niland</u>
Na	8,100	47,100
Ca	1,360	22,700
K	1,050	12,000
Fe	9	240
Mn	-	625
Ba	14	140
Sr	320	-
Zn	-	160
Li	40	-
B	10	-
Pb	-	29
Mg	17	165
Cu ⁻	-	0.5
NH ₄ ⁺	41	-
Cl ⁻	15,850	131,200
CO ₂	200	-
SO ₄ ²⁻	43	-
TDS (calc)	27,050	214,400

Note: CO₂ includes carbonate in all forms

TABLE 3
CANDIDATE GEOTHERMAL CEMENT SYSTEMS

System No.	Basic Cement	Code	Amt.	Additives (% by weight of cement)						% H ₂ O	Slurry Density (lb/gal)
				Code	Amt.	Code	Amt.	Code	Amt.		
1	Kaiser Permanente "G"	R1	1.0	SAND	35	-	-	-	-	54	15.9
2	"	R1	1.0	SF	35	-	-	-	-	54	15.9
3	"	R1	1.0	SF	35	FA/N	79	-	-	93	15.1
4	"	R1	1.0	SF	35	PERL	8.5	BENT	2.0	116	13.5
5	"	R1	1.0	SF	35	NaCl	20	-	-	54	16.1
6	"	R1	1.0	SF	35	NaCl	5.4	-	-	54	16.0
7	"	R1	1.0	SF	35	KCl	20	-	-	54	16.1
8	"	R1	1.0	SF	35	KCl	5.4	-	-	54	16.0
9	"	R1	1.0	SF	35	DE	8.9	-	-	91	14.5
10	"	R1	1.0	SF	35	COAL	27	-	-	63	14.6
11	"	R1	1.0	SF	35	GILS	27	-	-	63	14.5
12	"	R1	1.0	SF	35	SMS	2.5	-	-	122	12.0
13	"	R1	1.0	SF	35	MSS	2.5	-	-	130	11.9
14	"	R1	1.0	SF	20	DE	20	-	-	125	12.3
15	"	R1	1.0	SF	35	NaCl	2.7	BENT	16	135	12.8
16	Unadeep "J"	R1	0.2	-	-	-	-	-	-	44	15.4
17	"	R1	0.4	-	-	-	-	-	-	44	15.4
18	"	R1	0.2	DE	8.9	-	-	-	-	81	13.5
19	"	R1	0.4	DE	8.9	-	-	-	-	81	13.5
20	"	R1	0.6	DE	8.9	-	-	-	-	81	13.5
21	"	R1	0.2	FA/N	79	-	-	-	-	75	15.0
22	"	R1	0.4	FA/N	79	-	-	-	-	75	15.0
23	"	R1	0.2	AP	50	-	-	-	-	98	13.8
24	"	R1	0.4	AP	50	-	-	-	-	98	13.8
25	"	R1	0.6	AP	50	-	-	-	-	98	13.8
26	"	R1	0.4	PERL	8.5	BENT	2.0	-	-	106	13.3
27	"	R1	0.2	BENT	4.0	-	-	-	-	65	14.2
28	"	R1	0.4	BENT	4.0	-	-	-	-	65	14.2
29	"	R1	0.2	BENT	8.0	-	-	-	-	86	13.1
30	"	R1	0.4	BENT	8.0	-	-	-	-	86	13.1
31	"	R1	0.2	NaCl	20	-	-	-	-	44	15.7
32	"	R1	0.2	KCl	5.4	-	-	-	-	44	15.5
33	"	R1	0.2	SMS	2.0	-	-	-	-	90	12.3
34	Ciment Fondu	R1	1.5	R2	1.5	-	-	-	-	50	15.3
35	"	R1	1.5	R2	1.5	FA/N	85	-	-	81	14.8

TABLE 3 (continued)

System No.	Basic Cement	Code	Amt.	Additives (% by weight of cement)						% H ₂ O	Slurry Density (lb/gal)
				Code	Amt.	Code	Amt.	Code	Amt.		
36	Ciment Fondu	R2	1.5	FA/N	85	-	-	-	-	81	14.8
37	"	R3	4.0	FA/N	85	-	-	-	-	81	14.8
38	Slag Cement	R1	1.3	SF	35	-	-	-	-	56	15.9
39	"	R1	1.3	SF	35	FA/N	79	-	-	93	15.1
40	"	R1	1.3	SF	35	SMS	1.5	-	-	122	12.8
41	"	R1	1.3	SF	35	PP	10	-	-	74	14.9
42	Lime & Silica (1:1)	R1	0.7	-	-	-	-	-	-	96	12.0
43	"	R1	1.0	AH	7.0	-	-	-	-	96	11.9
44	"	R1	0.7	PERL	8.5	BENT	2.0	-	-	110	10.8
45	"	R1	1.0	FA/N	79	-	-	-	-	130	11.8
46	"	R1	0.3	MgO	4.6	-	-	-	-	96	11.9
47	Lime & Silica (1:04)	R1	0.7	-	-	-	-	-	-	100	11.6
48	Millwhite Poz-Lime (1:0.42)	R1	0.7	-	-	-	-	-	-	142	10.8
49	Ideal "B"	R1	1.2	SAND	35	-	-	-	-	56	15.9
50	"	R1	1.5	SF	35	-	-	-	-	56	15.9
51	"	R1	0.6	SF	35	PERL	8.5	BENT	2.0	118	13.5
52	"	R1	1.0	SF	35	KCl	20	-	-	56	16.1
53	"	R1	1.0	SF	35	NaCl	20	-	-	56	16.1
54	"	R1	1.0	SF	35	FA/L	79	-	-	120	14.2
55	TXI Lightweight	SF	35	BENT	8	-	-	-	-	117	12.3
56	"	BENT	10	-	-	-	-	-	-	132	11.7
57	"	SF	35	PERL	8.5	-	-	-	-	148	12.0
58	"	PERL	8.5	-	-	-	-	-	-	122	12.0
59	"	DE	10	-	-	-	-	-	-	170	11.4
60	"	DE	10	PERL	8.5	-	-	-	-	200	11.2
61	Kaiser Permanente "G"	R1	1.8	SAND	35	FA/N	79	-	-	93	15.1
62	" "	R1	0.8	SF	100	-	-	-	-	72	16.0

TABLE 3 (continued)

Additive Codes

R 1 - retarder - proprietary blend of sugar and lignin derivatives
R 2 - retarder - proprietary blend of lignin and inorganic salts
R 3 - retarder - proprietary blend of lignin, sugar, and inorganic acid

SAND - silica sand, 100 μ m average particle size

SF - silica Flour, <10 μ m average particle size

DE - diatomaceous earth

FA/N - Needles Fly Ash

FA/L - La Due Fly Ash

AP - Airox Pozzolan

PERL - expanded perlite

BENT - bentonite

SMS - sodium metasilicate

MSS - modified sodium silicate

PP - plaster of paris

AH - aluminum hydroxide

COAL - powdered coal

GILS - gilsonite

TABLE 4
RESULTS OF INITIAL SCREENING PROGRAM

See Table 3 For System Compositions

System No.	Thickening Time 300°F BHCT (hr:min)	°C	Compressive Strength (psi)				Water Permeability 227°C, 3 days (md)	Bond Strength (psi)		% Expansion - 204°C	
			1 day	3 days	7 days	28 days		outside	inside	Test 1	Test 2
1	3:24	227 316	3390 4860	2300 -	5410 890	4350 5600	0.016	150	1500	-	0.12
2	+6:00	227 316	3590 5150	5000 -	7110 4550	2750 6880	<0.001	450	2400	0.13	0.14
3	+6:00	227 316	2520 3620	5350 -	6010 1440	5000 2930	<0.001	850	2350	0.17	0.12
4	+6:00	227 316	1610 1050	890 -	1410 1070	780 1800	0.05	150	700	0.19	0.19
5	+6:00	227 316	4130 3690	4710 -	4520 4870	1300 4330	0.04	225	1200	0.22	0.22
6	6:47	227 316	5190 6780	5350 -	2980 5280	2250 7950	0.01	250	2450	0.18	0.19
7	7:42	227 316	3360 3710	5030 -	6170 3890	2750 4780	0.03	425	2500	0.17	0.20
8	3:14	227 316	5030 4980	5990 -	6850 -	2300 5800	0.015	250	525	0.16	0.15
9	+6:00	227 316	- -	2870 -	2130 1920	2300 5600	0.058	100	850	0.15	0.17
10	+5:00	227 316	- -	2550 -	3140 1420	2750 5430	-	500	1275	0.15	0.18
11	+5:00	227 316	- -	3060 -	2380 760	2630 2880	<0.001	650	1775	0.20	0.22
12	+6:00	227 316	- -	- -	180 200	- -	-	-	-	-	-
13	0:38	227 316	- -	- -	- -	- -	-	-	-	-	-
14	+7:00	227 316	- -	1530 -	1570 -	- 640	0.069	-	-	-	-
15	+7:00	227 316	- -	- -	850 550	- -	-	-	-	-	-
16	0:36	227 316	- -	- -	- -	- -	-	-	-	-	-
17	6:00	227 316	4400 4110	5390 -	4300 4540	3230 4030	-	375	1725	0.21	0.23
18	0:54	227 316	- -	- -	- -	- -	-	-	-	-	-
19	0:50	227 316	- -	- -	- -	- -	-	-	-	-	-
20	0:36	227 316	- -	- -	- -	- -	-	-	-	-	-
21	1:05	227 316	- -	- -	- -	- -	-	-	-	-	-
22	6:00	227 316	240 2840	970 -	930 3700	3350 3190	0.03	175	675	0.00	0.07

TABLE 4 (continued)

System No.	Thickening Time 300°F BHCT (hr:min)	°C	Compressive Strength (psi)				Water Permeability 227°C, 3 days (md)	Bond Strength (psi)		% Expansion - 204°C	
			1 day	3 days	7 days	28 days		outside	inside	Test 1	Test 2
23	0:43	227 316	- -	- -	- -	- -	- -	- -	- -	- -	- -
24	0:42	227 316	- -	- -	- -	- -	- -	- -	- -	- -	- -
25	0:26	227 316	- -	- -	- -	- -	- -	- -	- -	- -	- -
26	3:18	227 316	60 520	- -	470 830	580 500	- -	25	350	0.20	0.22
27	1:12	227 316	- -	- -	- -	- -	- -	- -	- -	- -	- -
28	4:03	227 316	2100 730	2440 -	2020 900	1650 430	<0.001	0	70	0.27	0.19
29	1:47	227 316	- -	- -	- -	- -	- -	- -	- -	- -	- -
30	2:02	227 316	800 860	2100 -	2280 900	1650 650	<0.001	0	-	0.14	0.10
31	4:52	227 316	3900 3430	3630 -	2240 2690	2650 4780	<0.001	475	1250	0.12	0.12
32	+6:00	227 316	4130 3710	4140 -	5190 4060	1400 2180	<0.001	25	300	0.14	0.16
33	+6:00	227 316	430 700	380 -	930 1130	4130 780	0.30	150	1550	0.17	0.08
34	4:07	227 316	- -	990 -	- -	3350 1980	0.101	600	1600	0.00	0.02
35	+6:00	227 316	- -	- -	1370 1090	1200 1100	- -	- -	- -	- -	- -
36	0:30	227 316	- -	- -	- -	- -	- -	- -	- -	- -	- -
37	0:15	227 316	- -	- -	- -	- -	- -	- -	- -	- -	- -
38	+6:00	227 316	- 4340	1530 3450	3780 3980	2400 3750	<0.001	300	>2500	0.19	0.22
39	5:00	227 316	- 4590	4400 3580	1200 4600	2430 2290	<0.001	-	1900	0.15	0.14
40	+6:00	227 316	- 1070	- 1110	- 450	3400 1200	- -	450	1075	-	-
41	+5:00	227 316	- 2630	1590 1970	2890 1190	2630 2750	0.01	450	1750	0.20	0.20
42	-	227 316	- -	600 -	1180 660	3650 1280	0.304	600	1875	0.04	0.06
43	-	227 316	- -	800 -	900 730	- 530	0.106	-	-	-	-
44	-	227 316	- -	290 -	330 400	- 450	0.54	-	-	-	-
45	-	227 316	- -	2770 -	1980 1750	- 250	0.001	-	-	-	-
46	-	227 316	- -	410 -	600 450	- 580	0.01	-	-	-	-

TABLE 4 (continued)

System No.	Thickening Time 300°F BHCT (hr:min)	°C	Compressive Strength (psi)				Water Permeability 227°C, 3 days (md)	Bond Strength (psi)		% Expansion - 204°C	
			1 day	3 days	7 days	28 days		outside	inside	Test 1	Test 2
47	+6:00	227 316	- -	1390 -	1620 170	- 325	0.01	-	-	-	-
48	-	227 316	- -	1450 -	1000 190	- 580	-	-	-	-	-
49	3:19	227 316	- 6350	3000 4440	3410 5310	600 7400	0.035	25	375	0.07	0.10
50	+6:00	227 316	- -	5350 -	5860 2730	1350 6550	<0.001	75	100	0.16	0.17
51	+6:00	227 316	- -	500 -	1530 880	2280 700	0.07	275	1100	0.17	0.16
52	4:41	227 316	- 3250	2070 3430	3010 3750	2500 5430	0.005	350	2075	0.20	0.20
53	+6:00	227 316	- -	- -	- -	4380 4150	0.07	750	1450	0.22	0.25
54	4:51	227 316	- 4610	3410 4060	4790 -	380 2800	<0.001	100	350	0.24	0.20
55	-	227 316	- -	- 106	- -	- -	-	-	-	-	-
56	-	227 316	- -	- 83	- -	- -	-	-	-	-	-
57	-	227 316	- -	- 79	- -	- -	-	-	-	-	-
58	-	227 316	- -	- 150	- -	- -	-	-	-	-	-
59	-	227 316	- -	- 13	- -	- -	-	-	-	-	-
60	-	227 316	- -	- 10	- -	- -	-	-	-	-	-

TABLE 5
X-RAY ANALYSIS OF LABORATORY SCREENING PROGRAM
28 DAYS - CURED AT 316°C AND SATURATED STEAM PRESSURE

<u>System</u>	<u>Major</u>	<u>Minor</u>	<u>Low</u>
1	-----	Xonotlite	Rustumite
2	Xonotlite	-----	Calcite
3	Tobermorite	-----	Rosenhahnite
4	Xonotlite	-----	Calcite
5	Xonotlite	-----	Calcite
6	Xonotlite	-----	-----
7	Xonotlite	-----	Calcite
8	Xonotlite	-----	Calcite
9	Xonotlite	-----	Calcite
10	Xonotlite	-----	Calcite
11	Xonotlite	-----	Calcite
17	Quartz	-----	Calcite, scawtite, truscottite, xonotlite
22	Calcium, analcime	Reyerite	-----
26	Scawtite	-----	Truscottite
28	Scawtite	-----	Quartz, xonotlite, truscottite
30	-----	-----	Quartz, xonotlite, scawtite
31	-----	Xonotlite	Quartz, scawtite
32	-----	-----	Quartz, scawtite, xonotlite, truscottite
33	-----	Scawtite, truscottite	Xonotlite
34	$\text{Ca}_2\text{Al}_2\text{SiO}_7 \cdot \text{H}_2\text{O}$	-----	Plaster of paris, ettringite
37	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$	-----	Plaster of paris, $\text{Ca}_2\text{Al}_2\text{Si}_7\text{H}_2\text{O}$
38	Xonotlite	-----	-----
39	Tobermorite	-----	Calcium analcime
40	-----	Xonotlite, truscottite	-----
41	Xonotlite	-----	Scawtite
42	Xonotlite	-----	Calcite, Quartz
43	Xonotlite	-----	-----
44	-----	Quartz	Xonotlite, scawtite, truscottite
45	-----	-----	Truscottite, xonotlite, tobermorite
46	Xonotlite	-----	Quartz, truscottite
47	Tobermorite	-----	Rosenhahnite, calcite
48	-----	-----	Truscottite, calcite
49	Xonotlite	-----	Calcite
50	Xonotlite	-----	Calcite

TABLE 5 (continued)

<u>System</u>	<u>Major</u>	<u>Minor</u>	<u>Low</u>
51	Xonotlite	-----	Calcite
52	Xonotlite	-----	Calcite
53	Xonotlite	-----	Calcite
54	-----	Tobermorite	Truscottite

TABLE 6
COMPOSITION OF SYSTEMS CONTAINING SPECIAL ADMIXTURES

System No.	Basic Cement	Code	Amt.	Additives (% by weight of cement unless otherwise indicated)								%H ₂ O
				Code	Amt.	Code	Amt.	Code	Amt.	Code	Amt.	
S-1	Kaiser Permanente "G"	R1	1.0	FL1	1.5	SF	35					54
S-2	"	R1	1.0	FL2	0.35gal/sk	SF	35	DIS	0.8			54
S-3	"	R1	1.0	FL4	1.5	SF	35	BENT	2.0	PERL	8.5	116
S-4	"	R1	1.0	FL4	1.5	SF	35	DE	10			91
S-5	"	R1	1.0	FL4	1.5	SF	100	SMS	2.0	NaOH	1.0	136
S-6	Ideal "B"	R1	1.0	FL3	1.5	NaCl	20					56
S-7	Unadeep "J"	R1	0.4	FL1	1.5							46
S-8	"	R1	0.4	FL2	0.35gal/sk	DIS	0.8					44

CODE: R-1 - retarder - proprietary blend of sugar and lignin derivatives

FL1

FL3 - fluid loss additives - proprietary cellulosic blends

FL4

FL2 - fluid loss additives - proprietary liquid water soluble polymer

SF - silica flour, <10 μ average particle size

DIS - dispersant

BENT - bentonite

PERL - perlite

DE - diatomaceous earth

SMS - sodium meta silicate

TABLE 7
PERFORMANCE OF SYSTEMS CONTAINING SPECIAL ADMIXTURES

System No.	Thickening Time 300 F BHCT (hr:min)	Compressive Strength (psi) 400 F		Water Permeability (md)	API Fluid Loss 240 F, 500 psi (cc/30 min)
		1 day	28 days		
S-1	+6:00	7600	3600	<0.01	85
S-2	+6:00	6000	3500	<0.01	35
S-3	+6:00	2060	1560	0.09	320
S-4	+5:00	2250	2000	0.10	380
S-5	+6:00	2560	940	0.04	1100
S-6	2:30	-	2690	<0.01	1000
S-7	+6:00	4380	3500	<0.01	34
S-8	+6:00	3810	2560	<0.01	36

TABLE 8
RESULTS OF SIMULATED GEOTHERMAL TESTING PROGRAM UTILIZING THE D-BETA

Conditions: 150°C (300 F)
Circulating brine (See Table 1)

System Compositions Given In Table 3

System No.	Compressive Strength (psi)				Water Permeability (md)				Depth Of Deterioration	
	14 days	28 days	3 months	15 months	14 days	28 days	3 months	15 months	(in @ 15 months)	
1	4000	5300	4230	2400	0.011	0.032	0.066	0.13	1/16	0.063
2	8400	10380	4950	2250	0.002	0.009	0.012	0.011	1/20	0.050
3	4830	4230	3700	2180	0.004	0.035	0.039	0.024	1/16	0.063
4	1600	1100	850	15	0.072	0.098	0.15		1/2	0.500
5	5500	4250	3030	1280	0.003	0.062	0.081	0.11	1/20	0.050
6	7200	-	-	-	0.002	-	-	-	-	-
7	8025	-	-	-	0.013	-	-	-	-	-
9	3780	2600	2275	1250	0.053	0.044	0.12	0.42	1/4	0.250
10	4500	-	-	-	0.005	-	-	-	-	-
17	2700	3750	3380	2250	0.049	0.041	0.085	0.35	1/8	0.125
22	3580	2950	2400	1200	0.006	0.078	0.093	0.19	1/8	0.125
30	1500	2150	2200	broken	0.149	0.042	0.098	broken	-	-
43	1530	880	180	dis.	0.181	0.195	0.28	dis.	-	-
49	2150	2580	2550	5200	0.018	0.027	0.078	0.13	1/16	0.063
50	6400	5900	5400	5050	0.008	0.012	0.011	0.016	1/20	0.050
51	1750	1500	980	25	0.110	0.103	0.24	soft	3/8	0.375

TABLE 9
RESULTS OF FIELD TESTING AT EAST MESA TEST FACILITY

System	Compressive Strength (psi)				Water Permeability (md)				Size Reduction (%)				X-ray Diffraction Analysis		
	1 mo.	3 mo.	7 mo.	17 mo.	1 mo.	3 mo.	7 mo.	17 mo.	1 mo.	3 mo.	7 mo.	17 mo.	1 mo.	7 mo.	17 mo.
1	2830	500	2790	270	0.03	0.002	0.03	0.02	6	12	25		CC,-C ₂ SH	C ₂ SH,CH,A	CC,Ar,Q
2	1500	900	-	160	0.01	0.001	-	0.08	6	12	-		Q,CC	C ₂ SH,CH,A	CC,Ar,T
3	2250	1400	1510	1050	0.02	0.01	0.02	0.08	6	12	19		CC,Q	C ₂ SH,CH,A	Q,CC,Ar,T
5	880	1400	1920	340	0.06	0.01	0.18	0.05	6	12	19		CC,G	C ₂ SH,CH,A	CC,Ar,T
6	1250	1200	2160	1110	0.05	0.01	0.005	0.03	6	12	19		CC,Q	C ₂ SH,CH,A	CC,Ar,Q,T,X
9	2800	1480	2150	63	0.06	0.04	0.01	0.64	12	25	31		CC,T	C ₂ SH,CH,A	CC,Q,X
10	1730	1830	1680	1000	0.08	0.16	0.06	0.08	6	12	25		CC,Q	C ₂ SH,CH,A	CC,Ar,Q,X
17	2700	3750	4130	1020	0.18	0.41	0.03	0.35	6	12	37		CC,Q	CH, C ₂ SH	CC,Q,Ar,X
22	1830	780	1820	240	0.10	0.35	0.001	0.20	12	19	37		CC,Q	CH, C ₂ SH	QCC,X,Tr
49	2500	780	1420	1430	0.01	0.01	0.02	0.02	0	6	37		CC,Q	C ₂ SH,CH,A	CC,Q,Ar,X
50	2030	1250	1800	420	-	0.006	0.02	0.03	6	12	37		Q,CC	CH, C ₂ SH	CC,Ar,Q,X
52	1830	880	870	730	0.04	0.09	0.02	1.24	6	19	37		CC,Q	C ₂ SH,CH,A	CC,Q,Ar,X
53	2830	980	-	-	0.04	0.002	0.21	-	6	19	37		CC,Q	C ₂ SH,CH,A	CC,Ar,Q,T
54	1530	780	1180	200	0.08	0.45	0.02	0.31	6	19	25		CC,Q	CH, C ₂ SH	CC,Q,Ar,T
61	3580	1000	-	110	0.04	0.01	0.08	1.00	6	12	12		CC,Q	C ₂ SH,CH,A	Q,CC,Ar,T,X
62	-	680	2450	910	-	0.07	0.08	0.40	3	12	37		CC,Q	C ₂ SH,CH,A	Q,CC,Ar,X

Abbreviations: C₂SH - alpha dicalcium silicate hydrate

CH - portlandite, Ca(OH)₂

CC - calcite

Q - quartz

X - xonotlite

A - alite

Ar - aragonite

Tr - truscottite

T - tobermorite

TABLE 10
RESULTS OF FIELD TESTING AT NILAND TEST FACILITY

System	Compressive kPa	Strength psi	Water Permeability (md)	Phases Detected By X-ray Diffraction		Trace
				Major	Minor	
1	13500	1950	cracked	calcite, quartz	halite	
2	23500	3380	cracked	xonotlite	halite	anhydrite
3	13900	2000	cracked	quartz, calcite	halite, aragonite	
5	33800	4870	0.001	xonotlite	tobermorite, quartz, calcite	
6	15800	2270	0.362	xonotlite, calcite	quartz	
9	11800	1700	cracked	calcite, xonotlite	halite, aragonite	
10	11300	1630	cracked	calcite, xonotlite	halite, anhydrite	
17	18300	2630	cracked	calcite, quartz	halite	
22	10400	1500	cracked	quartz, calcite	galena (PbS)	
49	19100	2750	cracked	xonotlite, calcite halite	anhydrite	
50	23900	3440	cracked	xonotlite	halite, anhydrite	
52	13900	2000	cracked	xonotlite	tobermorite, halites	
53	14800	2130	cracked	xonotlite	halite	
54	30300	4360	0.106	calcite, quartz	aragonite, halite, galena	
61	24500	3530	0.018	calcite, quartz	halite, aragonite	
62	cracked		0.060	quartz, calcite	halite	

TABLE 11
TEST RESULTS FOR FURFURYL ALCOHOL/COAL SYSTEM

System	Composition	Thickening Time* 300 F BHCT (hr:min)	Slurry Condition	Compressive Strength (psi)			Water Permeability (mD)			Slurry Density (lb/gal)
				light brine (325°C) 7 days	dry heat (325°C) 28 days	dry heat (325°C) 28 days	light brine (325°C) 7 days	dry heat (325°C) 28 days	dry heat (325°C) 28 days	
1	Neat Furfuryl Alcohol	6:00+	poured out	-	-	-	-	-	-	-
2	Furfuryl Alcohol + 2.4% Tartaric Acid Solution (50%)	0:58	set	-	-	-	-	-	-	-
3	48.8% Furfuryl Alcohol 48.8% Powdered Coal 2.4% Malic Acid Solution (50%)	0:31	set	-	-	-	-	-	-	-
4	50.0% Furfuryl Alcohol 50.0% Powdered Coal	6:10	set	-	-	-	-	-	-	-
5	31.0% Furfuryl Alcohol 31.0% Experimental Resin 4607 37.0% Coal (<20 mesh) 1.0% ZnCl ₂ Solution (50%)	2:25	set	-	-	-	-	-	-	-
6	31.25% Furfuryl Alcohol 31.25% Experimental Resin 4607 37.0% Coal (<20 mesh) 0.5 ZnCl ₂ Solution (50%)	4:15	set	5225	4200	burned	0.004	0.001	burned	10.5
7	31.4% Furfuryl Alcohol 31.4% Experimental Resin 4607 37.0% Coal (<20 mesh) 0.2% ZnCl ₂ Solution (50%)	6:25	set	4150	-	burned	0.003	-	burned	10.6

*API Liner Cementing Schedule 30M

TABLE 12
GLASS TRANSITION TEMPERATURES OF SELECTED POLYMERS

<u>Polymer</u>	<u>Tg(°C)</u>	<u>Thermal Degradation Temp. (°C)</u>	<u>Reference</u>
Polystyrene ^a	100	300-400	45
Epoxide resin ^b	200-300	200	44
Polyurethane ^c	-	<225	46

a - crosslinked with divinylbenzene

b - bisphenol A + epichlorohydrin crosslinked with an alkylamine

c - tolylene diisocyanate + polytriol

TABLE 13
COMPOSITIONS OF ULTRA LIGHTWEIGHT CEMENT SLURRIES CONTAINING GLASS BUBBLES

<u>System No.</u>	<u>API Cement Class</u>	<u>% Silica Flour</u>	<u>Glass Bubble Grade</u>	<u>Slurry Density</u>	
				<u>kg/L</u>	<u>lb/gal</u>
GB1	G	35	1	1.26	10.5
GB2	G	35	1	1.32	11.0
GB3	G	35	1	1.40	11.7
GB4	G	35	1	1.54	12.9
GB5	G	35	2	1.28	10.7
GB6	G	35	2	1.36	11.3
GB7	G	35	2	1.45	12.1
GB8	G	35	2	1.57	13.1
GB9	G	0	1	1.20	10.0
GB10	G	20	1	1.20	10.0
GB11	G	0	1	1.14	4.5
GB12	G	10	1	1.14	9.5
GB13	G	20	1	1.14	9.5
GB14	G	0	1	1.08	9.0
GB15	G	5	1	1.08	9.0
GB16	G	20	1	1.08	9.0
GB17	A	10	1	1.07	8.95
GB18	A	20	1	1.08	9.0
GB19	A	25	1	1.08	9.0
GB20	A	30	1	1.08	9.0
GB21	A	35	1	1.08	9.0

TABLE 14
RESULTS OF TESTING ULTRA LIGHTWEIGHT GLASS BUBBLE CEMENTS
(SPECIMENS EXPOSED TO FRESH WATER)

System	1 Month Compressive Strength (psi)				3 Month Compressive Strength (psi)				1 Month Water Permeability (md)				3 Month Waterability Permeability (md)			
	300 F Circ.	300 F Stat.	420 F Stat.	600 F Stat.	300 F Circ.	300 F Stat.	420 F Stat.	600 F Stat.	300 F Circ.	300 F Stat.	420 F Stat.	600 F Stat.	300 F Circ.	300 F Stat.	420 F Stat.	600 F Stat.
GB 1	875	1675	850	950	crumbled	870	550	550	0.14	0.003	0.11	0.19	crumbled	0.002	0.12	0.29
GB 2	900	1825	800	875	100	750	640	775	0.13	0.001	0.14	0.16	soft	0.003	0.15	0.16
GB 3	1475	1175	550	1400	740	775	650	950	0.12	0.031	0.17	0.10	0.68	0.010	0.15	0.049
GB 4	3875	2800	700	2950	1370	1350	2150	3050	0.17	0.006	0.42	0.10	0.27	0.003	0.093	0.057
GB 5	300	975	350	700	soft	175	100	775	0.52	0.011	0.25	0.19	soft	0.017	0.19	0.27
GB 6	600	950	450	850	75	375	360	750	0.45	0.037	0.24	0.20	soft	0.004	0.12	0.067
GB 7	1250	2225	900	1200	740	750	300	1175	0.25	0.015	0.29	0.39	1.43	0.008	0.27	0.074
GB 8	3050	2775	975	1900	750	2125	690	1550	0.12	0.002	0.24	0.22	0.75	0.007	0.31	0.099
GB 9	--	190	120	25	--	175	110	50	--	0.024	0.00	soft	--	soft	soft	soft
GB 10	--	1300	375	375	--	825	850	550	--	0.004	0.58	0.56	--	0.003	0.037	0.80
GB 11	--	500	50	25	--	220	50	50	--	0.010	25.0	soft	--	soft	soft	soft
GB 12	--	1275	25	325	--	1000	125	625	--	0.005	7.9	0.72	--	0.021	0.62	0.89
GB 13	--	1000	700	550	--	700	1200	625	--	0.001	0.29	0.23	--	0.017	0.17	0.54
GB 14	--	625	25	soft	--	525	25	25	--	0.011	soft	soft	--	0.17	soft	soft
GB 15	--	1100	25	230	--	1100	25	425	--	0.002	soft	0.82	--	0.009	soft	1.07
GB 16	--	600	975	820	--	440	1150	675	--	0.005	0.11	0.27	--	0.012	0.20	0.64
GB 17	--	975	--	550	--	750	--	625	--	0.002	--	0.90	--	0.004	--	0.68
GB 18	--	825	--	975	--	325	--	625	--	0.008	--	0.67	--	0.050	--	0.72
GB 19	--	900	--	975	--	350	--	875	--	0.014	--	0.42	--	0.054	--	0.25
GB 20	--	725	--	600	--	175	--	500	--	0.029	--	0.68	--	0.110	--	0.51
GB 21	--	850	--	315	--	575	--	225	--	0.002	--	0.97	--	0.009	--	1.85

TABLE 15
PERFORMANCE OF PROPOSED GEOTHERMAL CEMENT SYSTEMS

Slurry Composition	Thickening Time (min)	Fluid-Loss 240 F - 500 psi (cc/30 min)	Compressive Strength 400 F		Permeability (md)
			1 Day (psi)	28 days (psi)	
1. Class G + 35% silica flour + 1% lignin/sugar retarder + 1.5% cellulosic fluid-loss additive + 54% H ₂ O	+360	85	7595	3625	0.01
2. Class G + 35% silica flour + 1% lignin/sugar retarder + 0.35 gal/sk liquid fluid-loss additive + 0.8% dispersant + 54% H ₂ O	+360	35	6000	3500	0.01
3. Class B + 35% silica flour + 1% lignin/sugar retarder + 1.5% cellulosic fluid-loss additive + 56% H ₂ O	150	1000	NS	2687	0.01
4. Class J + 1.5% cellulosic fluid-loss additive + 0.4% lignin/sugar retarder + 44% H ₂ O	+360	34	4375	3500	0.01
5. Class J + 0.35 gal/sk liquid fluid-loss additive + 0.8% dispersant + 0.4% lignin/sugar retarder + 44% H ₂ O	+360	36	3810	2562	0.01
6. Class G + 35% silica flour + 2% bentonite + 8.5% perlite + 1.5% cellulosic fluid-loss additive + 1.0% lignin/sugar retarder + 116% H ₂ O	+360	320	2060	1562	0.09
7. Class G + 35% silica flour + 10% diatomaceous earth + 1.5% cellulosic fluid-loss additive + 1.0% lignin/sugar retarder + 91% H ₂ O	+360	380	2250	2000	0.10
8. Class G + 100% silica flour + 2% silica extender + 1.0% lignin/sugar retarder + 1.5% cellulosic fluid-loss additive + 1.0% NaOH + 136% H ₂ O	+360	1000	2560	937	0.04

TABLE 16
PARTICLE SIZE AND CALCULATED SURFACE AREA OF CEMENTS AND SILICAS

<u>Designation</u>	<u>Average Particle Size</u>		<u>Calculate Surface Area Sq. cm/gm</u>
	<u>Av. Mesh</u>	<u>Av. Micron*</u>	
70-200 mesh sand	70-200	105	215
Silica Flour	< 325	15	1510
180 μ m silica	70-200	175	125
120 μ m silica	100-170	120	190
60 μ m silica	100-325	60	375
30 μ m silica	< 325	32	710
10 μ m silica	< 325	10.5	2150
3 μ m silica	< 325	3.2	7075
Class A Blaine Sedigraph	< 325	7.4	2565
	< 325	19.5	2482
Class B Blaine Sedigraph	< 325	6.3	2992
	< 325	13.5	3009
Class G Blaine Sedigraph	< 325	5.6	3390
	< 325	14.0	2858
Class H Blaine Sedigraph	< 325	8.8	2158
	< 325	27.0	1878
Slag Cement Blaine Sedigraph	< 325	3.8	4996
	< 325	7.5	4308

* The Blaine average size is a number average.
 The Sedigraph average size is a weight average.
 Blaine size was used for the silicas.

TABLE 17
COMPOSITIONS OF SLURRIES STUDIED FOR EFFECTS OF SILICA PARTICLE SIZE

<u>Figure No.</u>	<u>Curve No.</u>	<u>Class Cement</u>	<u>Type Silica</u>	<u>% Silica</u>	<u>% Retarder</u>	<u>% Water</u>	<u>% Other</u>	<u>Weight lb/ft</u>
16	1	G	Flour	35	0.4	113	2B,8.5P	101
	2	G	Sand	40	0.4	102	2B,8.5P	102
17	1	G	Flour	35	0.3	102S*	2B,8.5P	102
	2&3	G	Sand	40	0.3	102S	2B,8.5P	102
18	1	G	Sand	40	0.3	102	2B,8.5P	102
	2	G	Sand	60	0.3	108	2B,8.5P	107
	3	G	Sand	80	0.3	114	2B,8.5P	111
19	1	G	Varies	40	0.4	54	--	120
	2	B	Varies	40	0.5	54	--	120
	3	H	Varies	40	0.4	50	--	122
20	1-4	G	Varies	40	0.4	54	--	120
21	1-4	G	Varies	35	0.3	102	2B,8.5P	102
22	1-4	G	Flour	35	0.4	54	20N	120
	2	G	Sand	40	0.4	54	20N	121
	3	G	Flour	35	0.3	102	2B,8.5P	106
					37N			
	4	G	Sand	40	0.3	102	2B, 8.5P	107
					37N			
23	1	None	Flour	100	0	125	44N	--
	2	None	Sand	100	0	125	3.7N	--
	3	None	Sand	100	0	125	44N +	--
	4	None	Sand	100	0	125	0.01C	--

*Symbols used in this table

Flour = Silica flour (average 15 μ m) sand = fine silica (average 100 μ m).

S = Salt (NaCl) water for percentage see Figure 2.

B = Bentonite

P = Expanded perlite (8.5P = approx. 1 cu. ft.)

N = Salt (sodium chloride)

C = Calcium hydroxide (lime) approx. saturated at 260°C.

TABLE 18
X-RAY ANALYSIS OF SILICA STABILIZED PORTLAND CEMENTS

<u>Sieve</u>	<u>Silica Size Micron</u>	<u>Major</u>	<u>Phases Detected Minor</u>	<u>Trace</u>
70-100	175	α -quartz scawtite	Kilchoanite -	Xonotlite anhydrite
100-170	120	α -quartz Kilchoanite	-	anhydrite
170-325	60	Kilchoanite	-	Xonotlite
< 325	32	Xonotlite	-	α -quartz
< 325	10.5	Xonotlite	-	Kilchoanite α -quartz
< 325	3.2	Xonotlite	-	Scawtite
70-200	105	α -quartz Kilchoanite	Calcio- Chondroite	-
< 325	15	Xonotlite	-	Scawtite anhydrite

TABLE 19
CEMENT SLURRY COMPOSITIONS REPORTED
ADDITIVES (% BWOC)

Figure No.	System No.	Basic Cement	Silica Flour, %	Retarder, %	Other*, %	Other*, %	%H ₂ O	Slurry g/cm ³	Density lb/gal
25	1 and 2	Class G	35	0.8	--	--	54	1.90	15.8
25	3 and 4	Class G	35	0.8	PERL 8	BENT 3	125	1.56	13.0
26	1 and 2	Class G	100	0.8	NaOH 1	--	70	1.92	16.0
26	3	Class G	25	0.8	HS 75	--	185	1.50	12.5
26	4	Class G	100	0.8	BENT 12	--	200	1.50	12.5
27	1 and 2	Class G	70	2.0	NaOH 20	--	65	1.92	16.0
27	3 and 4	Class G	55	2.0	NS ₃ 32	--	180	1.50	12.5
29	1	Class G	18	2.0	NS ₂ 70	--	75	1.88	15.7
29	2	Class G	18	2.0	NS ₂ 70	NS 2	125	1.64	13.7
29	3	Class G	18	2.0	NS ₂ 70	NS 4	175	1.57	12.6

*Additive Codes:

PERL - Expanded perlite	NS ₃ - Sodium silicate, Na ₂ O 3.3 SiO ₂
BENT - Bentonite (gel)	NS ₂ - Sodium silicate, Na ₂ O 2.0 SiO ₂
NaOH - Sodium hydroxide	NS - Sodium metasilicate, Na ₂ O SiO ₂
HS - Hydrous silica (e.g. silica gel)	

FIGURE 1 - DIAGRAM OF A CASING CEMENTING JOB

FIGURE 2 — Block Diagram of Screening Program for Candidate Geothermal Cement Systems.

**FIGURE 3 - PHOTOGRAPHS
OF SLEEVES FOR
MEASUREMENT
OF CEMENT
EXPANSION**

FIGURE 4 SCHEMATIC DIAGRAM OF DYNAMIC BRINE EXPOSURE TESTING APPARATUS (D-BETA)

KEY TO ABBREVIATIONS:

BPR = Back Pressure Regulator
 PI = Pressure Indicator
 PR = Pressure Recorder
 PT = Pressure Transducer
 TE = Temperature Element
 TI = Temperature Indicator
 TR = Temperature Recorder
 TT = Temperature Transducer
 + = Flow to Cores
 # = Flow from Cores to Reservoir

**FIGURE 5 - MAP SHOWING LOCATION OF EAST MESA
AND NILAND GEOTHERMAL TEST SITES**

Courtesy of Westec Services, Inc.

FIGURE 6
PHOTOGRAPH OF DYNAMIC BRINE
TESTING APPARATUS AT EAST
MESA, CALIFORNIA

FIGURE 7 — Compressive Strength Behavior of Selected Candidate Cement Systems at 227 and 316°
28 Days Curing Time

FIGURE 8 — Differential thermal analysis of cement cured 28 days at 600°F. All systems retarded for placement time. Deltatherm D2000, heat rate = 10°C/min, $\Delta T = 1^\circ\text{C}/25.4\text{mm}$ ($\frac{1}{2}$ scale simulated thermograms).

**FIGURE 9 - PHOTOGRAPH OF SCALE FORMATION
ON D-BETA CEMENT SPECIMEN**

GEOTHERMAL TEST WELLS, EAST MESA TEST SITE

**Figure 10. Phantom View of East Mesa Test Wells
(Courtesy of Bureau of Reclamation)**

FIGURE 11 — Differential Thermal Analysis of Cement Systems Cured 7 months at the East Mesa Test Site (Deltatherm D2000, 1°C/in. sensitivity, 10°C/min heat rate)

**FIGURE 12 - SEM PHOTOGRAPHS OF EAST MESA CEMENT
SPECIMENS, 17-MONTHS EXPOSURE**

**PHOTO #1
System 1**

**PHOTO #2
System 1**

FIGURE 12 CONT'D **PHOTO #3
System 2** **PHOTO #4
System 2**

FIGURE 12 CONT'D **PHOTO #5
System 3** **PHOTO #6
System 3**

FIGURE 12 CONT'D **PHOTO #7
System 5** **PHOTO #8
System 5**

FIGURE 12 CONT'D **PHOTO #9
System 6** **PHOTO #10
System 6**

FIGURE 12 CONT'D

PHOTO #11
System 9

PHOTO #12
System 10

FIGURE 12 CONT'D **PHOTO #13
System 10** **PHOTO #14
System 17**

FIGURE 12 CONT'D

**PHOTO #15
System 22**

**PHOTO #16
System 22**

FIGURE 12 CONT'D **PHOTO #17**
System 49 **PHOTO #18**
System 49

FIGURE 12 CONT'D **PHOTO #19**
System 50 **PHOTO #20**
System 52

FIGURE 12 CONT'D **PHOTO #21**
System 53 **PHOTO #22**
System 54

FIGURE 12 CONT'D

**PHOTO #23
System 61**

**PHOTO #24
System 61**

FIGURE 12 CONT'D **PHOTO #25**
System 62 **PHOTO #26**
System 62

FIGURE 13 — Schematic Diagram of Niland Test System

FIGURE 14 — Differential Thermal Analysis of Cement Systems Cured 38 days at the Niland Test Site (Deltatherm D2000, 1°C/in. sensitivity, 10°C/min heating rate).

FIGURE 15 - APPARENT VISCOSITIES OF MUD, CEMENT AND SPACER COMBINATIONS

Fig. 16 - Effect of silica type on strength of lightweight cements aged in brine.

Fig. 17 - Effect of salt in mix water on strength and permeability at 325°C.

Fig. 18 - Effect of the amount 70-200 mesh silica (based on portland cement) added to lightweight cement aged in heavy brine at various temperatures.

Fig. 19 - Effect of silica particle size on degradation of various cements (normal weight).

Fig. 20 - Effect of silica particle size on degradation of normal weight Class G cement at various temperatures.

Fig. 21 - Similar to Fig. 20 except using lightweight cement.

Fig. 22 - Effect of temperature on normal (nor) and lightweight (L.W.) cements cured in heavy brine.

Fig. 23 - Effect of brine composition on solution of silica in brines at 260°C (500°F).

Fig. 24 - Strength and permeability of xonotllite cement systems at temperatures of 150-175°C.

Fig. 25 - Effect of circulating and static brines on xonotllite cement: 1) 16 lb/gal in static brine; 2) 16 lb/gal in circulating brine; 3) 13 lb/gal in static brine; 4) 13 lb/gal in circulating brine.

Fig. 26 - Effect of brines on truscottite cements (formulations in Table 19): 1) 16 lb/gal in static brine; 2) 16 lb/gal in circulating brine; 3) 12.5 lb/gal in static brine; 4) 12.5 lb/gal which did not produce truscottite.

Fig. 27 - Effect of brines on pectolite (formulations in Table 1): 1) 16 lb/gal in static brine; 2) 16 lb/gal in circulating brine; 3) 12.5 lb/gal in static brine; 4) 12.5 lb/gal in circulating brine.

Fig. 28 - Effect of scawtite concentration on xonotllite-type cements: 1) portland cement -232°C, 7 days; 2) Class J cement -325°C, 28 days.

Fig. 29 - Effect of static brine on truscottite-pectollite combinations: 1) 15.7 lb/gal; 2) 13.7 lb/gal; 3) 12.6 lb/gal.

Fig. 30 - EDX plot showing peaks of silicon and calcium.

Fig. 32 - Truscottite crystals determined by EDX and x-ray diffraction.

Fig. 33 - Truscottite crystals occurring in cement pore spaces.