CEMENTING OF GEOTHERMAL WELLS

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Abstract

A coordinated program for the development of improved cements specifically designed for geothermal well applications was started in April 1976. Since that time an assessment of the state of the art of well cementing has been made, a management plan prepared, and research on organic and inorganic cementing materials started. Work accomplished during the period April 1-June 30, 1977 is described in the current report.

Summary

Work to implement the program plan for the development of improved high temperature cementing materials for geothermal wells is continuing. Research work is currently in progress at Brookhaven National Laboratory, Colorado School of Mines, Dowell, and the National Bureau of Standards. Based upon the response from an RFP, contracts are being awarded to Battelle's Columbus Laboratories, Pennsylvania State University, and the University of Rhode Island. It is planned to award one additional contract. When the latter is initiated, the first three elements in the program management plan (problem definition, materials development, and property verification) will be implemented.

Cementing of Geothermal Wells

Progress Report No. 5

April-June 1977

Introduction

In April 1976, the ERDA Division of Geothermal Energy initiated a program for the development of improved cements specifically designed for geothermal well applications. The motivation for the program stems from an assessment that the cements currently used deteriorate in the geothermal environments, and that the life expectancy of a geothermal well, and therefore the economics of geothermal processes, can be improved significantly if better materials are developed.

The cements presently used to complete geothermal wells are similar to those used in oil and gas wells. These materials deteriorate in geothermal environments and the failure of several wells has been attributed to cement degradation. Total loss of a well can result in a loss of up to \$1,000,000. A partial well failure due to inadequate cement can result in an energy production decline or environmental damage. Thus, a real economic need exists for the development of improved cementing materials.

For use in geothermal wells, cementing materials with the following characteristics are needed.

1. Compressive strength, > 1000 psi 24 hours after placement.
2. Permeability to water, < 0.1 milli Darcy.
3. Bond strength to steel casing, > 10 psi.
4. Stability, no significant reduction in strength or increase in permeability after prolonged exposure at 400°C (~ 750°F) to 25% brine solutions, flashing brine, or dry steam.

5. Placement ability, capable of 3 to 4 hr retardation at expected placement temperatures.
6. Compatibility of the cement with drilling mud.
7. Non-corrosive to steel well casing.

The Process Technology Division of the Department of Applied Science at BNL is assisting the Division of Geothermal Energy in developing and managing a program that will result in the development of materials meeting the criteria listed above. The program represents an integrated approach to the definition, development, and implementation of the work. A successful development of improved materials will lead to a major advance in the technology required to economically utilize geothermal energy.

The goals for the overall program are as follows:

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

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

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

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

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

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

3. Develop the technology required to mix, pump, and place the cementing material.
4. Demonstrate the process by the cementing of a prototype well.
5. Perform cost analyses to determine the economic viability of the cementing systems under investigation.
6. Involve the well-cementing service industry and well owners in all phases of the program in order to provide a technical basis for the rapid implementation of the technology.
7. Prepare a comprehensive, high-temperature geothermal well-cementing manual which will include details of down-hole equipment, pumps cement properties, and field examples.

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

This report constitutes the fifth in a series of quarterly reports describing work performed at BNL on the program. Accomplishments during the period April-June 1977 are summarized below. During the quarter work has been performed in Tasks 1, 2, 3, and 7. Work on other Tasks will commence as additional research contracts are awarded.

Task 1. Program Management Plan

The need for ERDA to sponsor a program to develop improved geothermal cementing materials was ascertained by evaluating information obtained from well owners, cementing service companies, and governmental and private research organizations. The consensus of those contacted was that the program should be a cooperative one performed on a cost-sharing

basis with well cementing service companies and well owners. It was also established that the focal point of a program should be a series of down-hole test facilities. Testing should be performed in several geothermal environments but the highest priority for near-term (~ 10 yr) application should be given to medium salinity brines at temperatures up to 400°C (750°F).

In an earlier progress report,¹ an outline of a proposed management program was presented. The program consisted of the following elements: problem definition, materials development, property verification, down-hole testing, and the use of the cements in completing demonstration wells. The proposed program was approved by the DGE and work to implement it is in progress.

During the previous report period² the first two contracts for research on high temperature inorganic cementing materials were initiated. Work at the Colorado School of Mines (CSM) to study calcium silicate cements was started on April 1, 1977. Progress to date is reported in Task 2 and Appendix 1.

The National Bureau of Standards (NBS) was selected to perform property verification tests. This work, described in Task 3, will be a precursor to down-hole evaluations.

During the current quarter, ERDA/DGE awarded a contract to Dowell, Division of the Dow Chemical Company, to perform research on high temperature cementing materials. BNL will be the technical monitors for this program.

A "Request for Proposal" (RFP) for additional research on high temperature well cementing materials was advertised in the "Commerce Business Daily" on March 4, 1977. The closing date for proposals was

May 2, 1977. A total of 60 copies of the RFP were distributed and 13 proposals were received. Review of the proposals has been completed and to date a contract has been awarded to the University of Rhode Island (URI) to study calcium aluminophosphate cements. Work will commence at URI during July.

Contracts will also be awarded to Battelle's Columbus Laboratories and Pennsylvania State University. Both programs will start in September. It is planned to award one additional contract by early FY 1978. With the awarding of this contract, the first three elements in the program management plan (problem definition, materials development, and property verification) will be fully implemented.

As a means of obtaining technical guidance for the overall program and as an initial step in the technology transfer process, BNL has established a "Geothermal Well Cement Advisory Panel". Representatives from many segments of the industry are represented on the panel. Current members are listed below.

L. E. Kukacka, Chairman, Brookhaven National Laboratory

D. Free, Dowell

J. P. Gallus, Union Oil of California Research

C. E. Johnson, Chevron Oil Field Research Company

G. L. Kalousek, Colorado School of Mines

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

D. K. Smith, Halliburton Services

S. M. Weiderhorn, National Bureau of Standards

The first meeting of the panel was held on May 26, 1977 at NBS in Washington, D.C. Reviews of the programs to be conducted by CSM and NBS

were given. The next meeting of the panel is tentatively scheduled for the first quarter of FY 1978.

Task 2. Selection of Well Cementing Materials

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

Polymer Cement

Polymer cements (PC) have been identified as promising well completion materials. Development of these materials is continuing at BNL. To date two monomer formulations, 60 wt% styrene - 40 wt% trimethylolpropane trimethacrylate (TMPTMA) and 50 wt% styrene - 33 wt% acrylonitrile-17 wt% TMPTMA, have been shown to be durable to geothermal fluids. Both systems can be polymerized using chemical initiators and heat or by chemical initiators and promoters. The former appears suitable for temperatures up to $\sim 150^{\circ}\text{C}$ (302°F) while the latter has given good results up to $\sim 240^{\circ}\text{C}$ (464°F).

The durability of PC to geothermal fluids has been found to be highly dependent upon the composition of the aggregate. Materials such as quartz, silica, fly ash, and portland cement have been investigated. All of the materials can be used in composites which have good durability at temperatures $< 218^{\circ}\text{C}$ (425°F). Above this temperature, only PC materials containing mixtures of silica sand and portland cement have been durable to brine and steam.³

To determine the reason for this effect, infra-red and Differential Thermal Analysis (DTA) studies are being performed. In these tests, each of the chemical constituents of Type III portland cement (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , and MgO) are being combined with silica sand and various vinyl-type monomers (MMA, TMPTMA, and styrene) to form PC.

Evidence of chemical bonding between the CaO and $-CH_2$ groups in the vinyl monomers has been detected using Infra-Red Spectroscopy. This is indicated by the transmittance ratio of $-CH_2$ groups to C=O groups which is reduced by half when the ratio of monomer to CaO is doubled. Similar effects are not noted when SiO_2 , Fe_2O_3 , and Al_2O_3 are used as the aggregate. Similar tests are currently being performed with samples that have been exposed in an autoclave to brine at $238^\circ C$ ($460^\circ F$). Preliminary data indicate that mixtures of CaO and Al_2O_3 yield the most durable composites. The optimum concentration of each of these materials will be determined.

Work to develop high temperature polymer formulations is continuing. In the previous report two monomer systems: 50 wt% styrene - 32.8 wt% acrylonitrile - 9 wt% TMPTMA - 8.2 wt% polyphenylene oxide, and 30 wt% styrene - 60 wt% triallyl cyanurate - 10 wt% polyphenylene oxide, were discussed. The decomposition temperatures for these materials in a nitrogen environment are $262^\circ C$ ($504^\circ F$) and $286^\circ C$ ($547^\circ F$), respectively.

During the current period PC specimens containing the two formulations were exposed to air at a temperature of $238^\circ C$ ($460^\circ F$) and to brine at $238^\circ C$ ($460^\circ F$) and $260^\circ C$ ($500^\circ F$). The styrene-acrylonitrile-TMPTMA-polyphenylene oxide system showed extensive degradation in the oven and in hot brine. After 60 days in brine at $238^\circ C$ ($460^\circ F$), the compressive strength decreased from a value of 10,500 psi to 2200 psi.

Considerably better results were obtained with the formulation containing styrene-triallyl cyanurate-polyphenylene oxide. Compared to the control compressive strength of 6372 psi, essentially no change in strength was detected after 30 days in an oven at $238^\circ C$ ($460^\circ F$). After

60 days in brine at the same temperature, the compressive strength was reduced to 4200 psi.

Good results were obtained when a PC formulation consisting of 17 wt% of a 80 wt% styrene - 8 wt% TMPTMA - 12 wt% polyphenylene oxide mixture was exposed to hot brine at 238°C (460°F). After 30 days in test, a strength of 11,074 psi was measured. The control value was 10,965 psi.

Work with styrene-acrylonitrile formulations containing acrylamide or methacrylamide was continued. Cross-linking agents (TMPTMA or divinyl benzene) are added to the monomers. Tests are being performed at temperatures up to 300°C (572°F). These formulations produce high quality composites with compressive strengths generally ranging between 20,000 and 25,000 psi and with water absorptions <0.5%. Good thermal stability and durability to hot brine has been observed. Preliminary indications are that the use of the formulations in conjunction with an aggregate containing from 20 to 30 wt% portland cement gives the maximum durability. Based upon the previously discussed indications of bonding between vinyl groups and CaO, the effect of the use of CaO and mixtures of CaO and Al_2O_3 on the durability will be ascertained.

Inorganic Cements

Research on high temperature inorganic cements is in progress at CSM. Work will commence at URI and Dowell in July and at Battelle and PSU in September. One additional contract will be initiated during FY 1978.

Colorado School of Mines (CSM)

The first quarterly report⁴ for the project is given in Appendix 1.

Dowell

Work to commence July 1977.

University of Rhode Island (URI)

Work to commence July 1977.

Battelle's Columbus Laboratories

Work to commence September 1977.

The Pennsylvania State University (PSU)

Work to commence September 1977.

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

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

PC specimens are currently being exposed to dry steam at 238°C at The Geysers. During the report period specimens were removed after exposure for 18 months. All appear to be in good condition (see Figure 1). Samples after exposure for 12 months are shown in Ref. 3. Evaluation of the samples is in progress. The next series of samples will be removed after exposure for 24 months.

A testing program that will be a precursor to down-hole evaluation has been started at the National Bureau of Standards. Test equipment is currently being assembled and tested. It is anticipated that samples will be placed into test during the last quarter of FY 1977.

Task 7. Administrative

During the current report period, three "Monthly Administrative Letters" were submitted to DGE and Quarterly Progress Report No. 4² was issued. A paper entitled, "The Applicability of Concrete Polymer Materials for Use in Geothermal Environments", was presented at the 1977 Society of Petroleum Engineers of AIME Symposium on Oilfield and Geothermal Chemistry in San Diego, California.

GEYSERS
18 MONTHS

Figure 1. PC samples after exposure at The Geysers
to dry steam at 238°C for 18 months.

References

1. Cementing of Geothermal Wells, Progress Report No. 2, July-September 1976, BNL 50578
2. Cementing of Geothermal Wells, Progress Report No. 4, January-March 1977, BNL 50657.
3. Cementing of Geothermal Wells, Progress Report No. 3, October-December 1976, BNL 50621.
4. Kalousek, G. L., Development of Cement for Use in Geothermal and Deep Oil Wells, First Quarterly Technical Report, April 15-July 1, 1977, BNL/ERDA Contract No. 406003-5, Colorado School of Mines.

Appendix 1

First Quarterly Technical Report, April 15, 1977 to July 1, 1977, BNL/ERDA Contract No. 406003-5, "Development of Cement for Use in Geothermal and Deep Oil Wells."

Introduction

The experimentation on the project has now been fully activated. The tests are essentially those described in the proposal relative to subject project. Compositions of 0.60 to 0.83 C/S, w/w Al_2O_3 , are autoclaved at 150 to 300°C and saturated steam pressure.

Materials and Tests

A proprietary cement, Unadeep, is the principal constituent of the mixes modified by additions of quartz (tripoli) and 0 to 7% Al_2O_3 as gibbsite. In anticipation of tests in saline waters, some of the mixes are treated with 2% Na_2O (as NaOH). Dwight Smith of Halliburton is forwarding 50 lbs of Type H cement, the same as that supplied to the National Bureau of Standards. Action has been initiated to obtain by-product gamma C_2S for the project.

Slurries of 0.46 W/S are cast into and cured in 1-inch cube molds for 24 hours at 150°C. A set of the cubes is tested in compression after this cure and the others are cured at 250 and 300°C for different periods of times. Selected cubes after testing are examined by X-RD for phase contents.

Results

The 7% Al_2O_3 substituted tobermorite, 0.83 C/(S + A), autoclaved at 250°C for 28 days did not undergo any alteration. It has been deter-

mined previously that Al_2O_3 - free tobermorite transformed to xonotlite above about 150°C with loss of strength. A companion specimen autoclaved at 300°C for 7 days transformed to xonotlite and truscottite/scawtite. The strength results at 300°C and higher temperatures as related to phase content will be determined.

The results on the mixes of 0.633 to 0.700 C/S with 0 to 7% Al_2O_3 confirmed the earlier qualitative findings that such compositions yield very high strengths at Al_2O_3 contents of 5 to 7%. Strengths from 10,000 to 13,000 psi were obtained on 250°C - 20 day specimens. Companion specimens autoclaved at 300°C for 7 days gave strength of about 6,000 psi except the 0.667 C/S product which had a strength of 10,000 psi.

A few 0.6 C/(S + A) mixes with 0.0 to 6.6% Al_2O_3 and cured for 7 days at 300°C gave strengths of 3,500 to 7,000 psi. The previous qualitative tests on similar paste specimens cured to an equilibrium condition showed very low strengths and truscottite - gyrolite intergrowths as binder. It appears that the present specimens will have to be cured for longer time and/or higher temperatures to ascertain definitely if the indicated binder is of low strength.

One immediate objective of the tests on cubes and small paste specimens is to determine the minimum temperature and time of autoclaving required for attainment of equilibrium. The truscottite is a case in point. This phase is the final C-S binder to coexist with excess silica at the high temperatures. Because of the large number of variables involved, a large number of tests would be required. Reducing the dwell time in the autoclaves will accelerate the progress of the program.

The studies at CSM have shown that metastable phases will be encountered and their occurrences could lead to wrong interpretations on the quality of the binder. The so called "3.15 A phase" of 0.83 C/S composition occurs frequently at about 250 to 300°C and has to be considered a metastable phase with respect to xonotlite (or scawtite in carbonated mixes). However, its persistence at about 250°C suggests it may have a narrow field of stability. Recent work under the NSF sponsored project has shown that C₂S-S cements at temperatures between about 150 and 300°C and compositions of 0.83 and 1.00 C/S form scawtite, a CO₂-bearing phase of reported composition 7 CaO·6 SiO₂·CO₂·3H₂O. Scawtite appeared as a stable phase in some of the cements studied. Reported observations on the phase indicate that CO₂ even in minute amounts stabilizes the structure. The formation of scawtite as an equilibrium phase has obvious implications. All commercial calcium silicate cements for use in cementing geothermal wells will most probably contain some CO₂. More information on relation between amount of CO₂ and scawtite formation will soon be available from the NSF sponsored project at CSM. Twelve samples, cements and products, are currently being analyzed at the P.C.A. Laboratories for CO₂. As soon as these results are available, a report entitled, "Hydrothermal Reaction of C₂S-S Cements," will be published.

George L. Kalonick