CEMENTING OF GEOTHERMAL WELLS

PROGRESS REPORT NO. 4
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PROCESS TECHNOLOGY DIVISION

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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 polymer cementing materials started. A contract for research on inorganic cementing materials has been awarded and others are planned. Work accomplished during the period January 1-March 31, 1977, is described in the current report.

Summary

Work to implement the program plan for the development of improved high temperature cementing materials for geothermal well applications is continuing. A contract to develop calcium silicate cements was awarded to the Colorado School of Mines. An RFP for additional work was prepared and advertised. Proposals are due on May 2, 1977. To the extent acceptable proposals are received, two or more programs will be funded.

The property verification phase of the program has been implemented by the selection of the National Bureau of Standards to perform screening tests on cementing materials. This work will be a precursor to down-hole evaluation.

Cementing of Geothermal Wells

Progress Report No. 4

January-March 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 power can be improved significantly if better materials are developed.

The cements 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 for geothermal wells.
3. Rapid transfer and implementation of the technology in the private sector.

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

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

Planning work to organize and develop a management plan designed to meet the above objectives was started in April 1976. Experimental and developmental 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 fourth in a series of quarterly reports describing work performed at BNL on the program. Accomplishments during the period January-March 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

Based upon information obtained from geothermal well owners, well cementing service companies, and governmental and private research organizations, the need for ERDA to sponsor a program to develop improved cementing materials has been ascertained. 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 750°F ($\sim 400^{\circ}\text{C}$).

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 current report period BNL awarded the first in a series of contracts for research on high temperature inorganic cementing materials. The contract is to study calcium silicate cementing materials and was awarded to the Colorado School of Mines for a period of 18 months starting April 1, 1977. Dr. G. L. Kalousek will be the Principal Investigator for the project.

A "Request for Proposal" (RFP) for additional research on high temperature well cementing materials was prepared, advertised, and copies sent to potential bidders. To date ~ 50 copies of the RFP have been distributed. Bids are due back on May 2, 1977. To the extent acceptable proposals are received, two or more programs will be funded. Current plans are to award the contracts during the last quarter of FY 1977.

The property verification phase of the program has been implemented by the selection of the National Bureau of Standards to perform screening tests on potential cementing materials. This work will be a precursor to down-hole evaluation.

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 cementing materials. Development of these materials is continuing at BNL. To date 2 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 styrene-TMPTMA mixture appears suitable for temperatures up to ~ 150°C (302°F) while the latter has given good results up to ~ 240°C (464°F).

The durability of PC to geothermal fluids has been found to be highly dependant upon the composition of the aggregate. Materials

such as quartz, silica, fly ash, and portland cement are being 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.

Differential thermal analysis (DTA) studies have been initiated during the current report period to determine why the addition of portland cement to silica sand aggregate results in improved durability. 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 in a PC formulation consisting of 12 wt% monomer (55 wt% styrene-36 wt% acrylonitrile-9 wt% TMPTMA) and 88 wt% aggregate (80 wt% sand-20 wt% portland cement constituent). DTA measurements are being performed before and after exposure in an oven to high temperature and to hot brine.

During the current report period, 2 monomer systems have been developed which may further extend the operating temperature range, but only limited testing has been performed. The onset of decomposition of polymer containing 50 wt% styrene-32.8 wt% acrylonitrile-9 wt% TMPTMA-8.2 wt% polyphenylene oxide is 262°C (504°F). The use of 30 wt% styrene in conjunction with 60 wt% triallyl cyanurate and 10 wt% polyphenylene oxide produces a polymer that starts to decompose at 286°C (547°F). Experiments to measure the strength and permeability of these systems after long-term exposure to hot brine have been started but test data are not yet available.

Experiments with several other monomer mixtures were also performed. These systems are as follows: styrene-acrylonitrile-acrylamide, styrene-acrylonitrile-methacrylamide, isobornyl methacrylate-methyl methacrylate, isobornyl methacrylate-methyl methacrylate-ethylthioethyl methacrylate, and isobornyl methacrylate-methyl methacrylate-acrylonitrile.

PC specimens consisting of 12 wt% of the monomers and 88 wt% of a sand-portland cement aggregate mixture were exposed in an oven at 238°C (460°F) for 30 days and to 25% brine at 260°C (500°F) for 10 days. Based upon the results from compressive strength and water absorption measurements, 2 formulations, 55 wt% styrene-40 wt% acrylonitrile-5 wt% acrylamide and 55 wt% styrene-37.5 wt% acrylonitrile-7.5 wt% methacrylamide, were selected for additional evaluation. Long-term testing has been started.

Inorganic Cements

Research contracts for the development of high temperature inorganic cementing materials will be awarded and monitored by BNL. To date a contract has been awarded to the Colorado School of Mines and an RFP has been advertised. This was discussed in Task 1.

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. After 1 year, good durability is indicated. The next

evaluation will occur during the next report period.

During the current report period, the National Bureau of Standards was selected to perform property varification tests. This work will be a precursor to down-hole evaluation. 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. 3² was issued. A paper entitled, "The Applicability of Concrete Polymer Materials for Use in Geothermal Environments", was accepted for presentation at the 1977 Society of Petroleum Engineers of AIME Symposium on Oilfield and Geothermal Chemistry.

References

1. Cementing of Geothermal Wells, Progress Report No. 2, July-September 1976, BNL 50578.
2. Cementing of Geothermal Wells, Progress Report No. 3, October-December 1976, BNL 50621.

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