CEMENTING OF GEOTHERMAL WELLS

PROGRESS REPORT NO. 3
OCTOBER - DECEMBER 1976

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. Plans to initiate research to develop inorganic cementing materials are being implemented. Work accomplished during the period October 1 - December 31, 1976, is described in the current report.

Summary

Technical discussions to determine the state of the art and the potential for new geothermal well cementing materials were continued. The consensus is that well cementing problems do exist and that an ERDA-sponsored program to develop improved materials is needed. Based upon this assessment, a program management plan has been prepared and work to initiate research to implement the program is in progress.

Research work on high temperature polymer cementing materials is progressing. A formulation containing a 55 wt % styrene - 36 wt % acrylonitrile-9 wt % trimethylolpropane trimethacrylate monomer mixture and an aggregate consisting of 50 wt % sand - 50 wt % portland cement appears stable at a temperature of 238°C (460°F). Several condensation-type polymers with high-strength characteristics at 300°C (572°F) have been identified and work to produce and characterize the materials is in progress. Studies to determine if the reactions can be initiated in the presence of sand and cement are also in progress.

Polymer specimens exposed to dry steam at a temperature of 238°C (460°F) for one year at The Geysers have shown good durability. Similar results were obtained previously at Baca Wells with samples tested in flashing brine at 160°C (320°F) for 180 days.

Cementing of Geothermal Wells

Progress Report No. 3

October-December 1976

Introduction

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

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 will represent an integrated approach

to the definition, development, and implementation of the work. A successful development of improved materials will lead to a major advance in the technology required to economically utilize geothermal energy.

The goals for the overall program are as follows:

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

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

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

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

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

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

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

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

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

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

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

Planning work to organize and develop a management plan designed to meet the above objectives was started in April 1976.¹ Experimental and developmental work was started during the transitional quarter.² 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 third in a series of quarterly reports describing work performed at BNL on the program. Accomplishments during the period October-December 1976 are summarized below. During the quarter work has been performed in Tasks 1, 2, 3, and 7. Work on other tasks will commence later in FY 1977 as research contracts are awarded.

Task 1. Program Management Plan

Technical discussions to determine the state of the art and the potential for new geothermal well cementing materials were continued. During the report period visits were made to the Shell Development Company and the National Bureau of Standards. Trip reports for these meetings have been submitted to the ERDA Division of Geothermal Energy (DGE).

Based upon the 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 the previous progress report,² 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 plan, schedule, and the estimated funding requirements were submitted to the DGE for review. Approval of the plan was obtained and work to implement it is in progress.

A preliminary "Program Research and Development Announcement" (PRDA) for high temperature cementing materials has been prepared and submitted to DGE. It is anticipated that this or a similar document (an RFP) will be issued by BNL during the next report period. To the extent acceptable proposals are received, two or more programs will be funded.

Task 2. Selection of Well Cementing Materials

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

Polymer cements (PC) have already been identified as potential well cementing materials. Development of these materials is continuing at BNL.

Previous work³ has shown the importance of aggregate composition on the durability and thermal stability of PC. Aggregate materials such as quartz, silica, flyash, and portland cement have been investigated. To date, only PC containing an aggregate consisting of silica sand and portland cement has been durable to brine and steam at temperatures $> 218^{\circ}\text{C}$ (425°F). This is illustrated in Figure 1. Below this temperature, specimens containing quartz, flyash, and silica sand have shown good durability.

During the current report period, an optimization of the sand-portland cement concentration in PC with respect to the thermal stability at 238°C (460°F) was performed. Three monomer systems consisting of styrene, acrylonitrile (ACN), and trimethylolpropane trimethacrylate (TMPTMA) were used in conjunction with the various aggregate mixtures.

Increased thermal stability with increasing portland cement concentration up to a maximum of 50% was noted. When a 50% sand-50% cement mixture was used in conjunction with a monomer mixture consisting of 55 wt.% styrene-36 wt.% ACN - 9 wt.% TMPTMA, essentially no change in strength occurred after a 30 day exposure at 238°C (460°F). Testing in a 25% brine solution at 260°C (500°F) is in progress.

The effects of various additives to the monomer system are also being determined. Increased thermal stability was obtained when a concentration of 10% n-phenyl maleimide by weight of monomer was added to the above system. The use of triallyl cyanurate in conjunction with polyester resins also shows promise of yielding a high temperature polymer cement. Triallyl cyanurate combines the functionality of three allylic groups with the

Figure 1. PC samples after exposure at The Geysers to dry steam at 238°C for 1 year. Samples 275-278 contain aggregate consisting of 90% sand - 10% cement. All others contain only sand.

triazine nucleus. This nucleus is one of the most thermally and chemically stable structures known.

Several condensation-type polymers with reported high-strength characteristics at 300°C (570°F) have been identified and work to produce and characterize the materials is in progress. Initially polyimides produced from pyromellitic dianhydride and the following will be evaluated; 4,4'-diaminodiphenyl ether, m-phenylenediamine, and p-phenylenediamine. Studies to determine if the reactions can be initiated in the presence of sand and cement and the effects of hydrolysis on the composites will also be performed.

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 PC materials are in progress. Tests are currently being performed in autoclaves containing brine at temperatures up to 260°C (500°F), and at well-head conditions at The Geysers. Low temperature (150°C)(300°F) tests are in progress at Raft River.

PC samples exposed to dry steam at 238°C (460°F) at The Geysers for one year have shown good durability (see Figure 1). This test is continuing. In a previous report³ results were given for tests in which samples were exposed to flashing brine at 160° (320°F) in a well at Baca Wells, New Mexico. After 180 days in test, little deterioration was apparent. Similar results have been obtained at Raft River.

Task 7. Administrative

During the current report period, three Monthly Administrative Letters have been submitted to DGE and Quarterly Progress Report No. 2² was issued. An abstract of a paper entitled "The Applicability of Concrete Polymer Materials for Use In Geothermal Environments" was submitted to the Society of Petroleum Engineers (SPR) for presentation at the "1977 SPE Symposium on Oilfield and Geothermal Chemistry".

References

1. Cementing of Geothermal Wells, Progress Report No. 1, April-June 1976, BNL 21609.
2. Cementing of Geothermal Wells, Progress Report No. 2, July-September 1976, BNL 50578.
3. Concrete-Polymer Materials for Geothermal Applications, Progress Report No. 9, April-June 1976, BNL 21665.

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