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Informal Report

Geothermal Materials Development

Annual Report FY 1990

Lawrence E. Kukacka

February 1991

Prepared for the
Geothermal Division
U.S. Department of Energy
1000 Independence Ave., S.W.
Washington, DC 20585

DEPARTMENT OF APPLIED SCIENCE

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Energy Efficiency and Conservation Division
Department of Applied Science
Brookhaven National Laboratory
Associated Universities, Inc.

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1. Executive Summary

Advances in the development of new materials, the commercial availabilities of which are essential for the attainment of Hydrothermal Category Level I and II Objectives, continue to be made in the Geothermal Materials Development Project. Many successes have already been accrued and the results transferred to industry. Private sector acknowledgement of this was made at Geothermal Program Review VIII which was held in April 1990. In the report of the Industrial Critique Panel on DOE Geothermal Fluid Handling, Panel Chairman, Mr. Olin Whitescarver of Unocal stated the following, "BNL presented the majority of work in the area of fluid handling. Most things that they have developed in the way of elastomers and materials of construction such as polymer concrete have become common place in our operations."[1]

In FY 1990, the R&D efforts were focused on reducing well drilling and completion costs and on mitigating corrosion in well casing. Activities on lost circulation control materials, CO_2 - resistant lightweight cements, and thermally conductive corrosion and scale - resistant protective liner systems have reached the final development stages, and cost-shared field tests are planned for the FY 1991-92 time frame. Technology transfer efforts on high temperature elastomers for use in drilling tools are continuing under Geothermal Drilling Organization (GDO) sponsorship. In the case of drillpipe protectors, increases in the operating capability for oil and gas applications have been achieved and the tool is being commercialized for those markets. Unfortunately, until suitable high temperature hydrolytically stable chemical bonding systems, needed to bond the elastomers to steel reinforcement, are developed, the tool will not meet geothermal requirements. Development of advanced bonding systems is a high priority activity in the 1991 Materials Project.

Development of advanced rotary head seals needed for geothermal drilling operations should be successfully completed in FY 1991. This device will also strongly impact oil and gas drilling.

Laboratory results indicate that mixtures of phosphate-modified calcium aluminate cements and hollow silliminite spheres produce promising CO_2-resistant well cementing materials. Retarders which result in the cement slurries meeting API pumpability standards have been identified, and downhole testing of cured samples in CO_2 containing brine at 320°C and pH~2.2 was started as a cost-shared program with DSIR in New Zealand. If tests scheduled for FY 1992 are successful, the Level III Objective of reducing well cement problems by 20% should be met.

Similar promise is being shown with chemical systems for lost circulation control. Depending upon the placement method selected, materials will be ready for field testing in late FY 1991. If successful, a major advance towards meeting Level III Objectives for reducing lost circulation episodes will have been made.

[1] Proc. DOE Geothermal Program Review VIII, San Francisco, April 1990, p. 191, DOE Conf-9004131, Washington, D.C., 1990.

Work on thermally conductive polymer cement liners for the corrosion protection of heat exchange tubing in binary plants has been slowed by delays in obtaining a field test site. This problem was solved late in FY 1990 and the program should be completed in FY 1991.

Preliminary cost-shared field tests performed at the Geysers with private sector steam producers established the technical feasibility for the use of polymer cement liners to provide corrosion protection for the upper portions of well casing and steam collection piping. Larger-scale tests are scheduled for FY 1991. If successful, wells that are being considered for shut-in due to unfavorable economics resulting from corrosion problems will continue to be operated, thereby helping to maintain electric generating capacity at the Geysers.

Without the successful completion of the above activities and others outlined in the FY 1991 AOP, the Level III Objectives for the Materials Development Project, and consequently the Level II Objectives for both the Conversion Technology and Hard Rock Penetration Tasks, will probably not be met.

2. Objectives

The Geothermal Materials Project is an important part of the Geothermal Division's (GD) Hydrothermal Category, and it has an impact on two tasks, Conversion Technology and Hard Rock Penetration. The objective of the project is to provide information to industry which will result in reduced costs of geothermal well-field and power-plant design, construction, and operation by (1) extending the operating range of equipment in terms of temperature limits and tolerance to chemically aggressive fluids, (2) extending equipment life, (3) reducing maintenance and replacement costs, and (4) substitution of lower cost materials. Specific goals to be achieved in realizing the objectives are to (1) reduce costs associated with lost circulation episodes by 30 percent in the near term, (2) reduce the costs of deep wells and directionally drilled wells by 10 percent in the near term, (3) reduce well-cementing problems for typical hydrothermal wells by 20 percent in the near term, and (4) reduce the cost of binary power cycles by development of a corrosion-resistant and low-fouling heat exchanger tube material costing no more than three times the cost of carbon steel in the near term.

2.1 Category

Level I Objective: Hydrothermal

Reduce the life-cycle cost of producing electricity from liquid-dominated hydrothermal resources to 3-7 cents/kWh in the mid-term.

2.2 Task: Conversion Technology

Level II Objectives: Although the Materials Project is structured as a project within the Conversion Technology Task, it is also making major contributions to the Hard Rock Penetration Task. Future commercialization within the Geopressured-Geothermal, Hot Dry Rock, and Magma Categories will also be highly dependent upon materials development.

For the Conversion Technology Task, the Level II Objectives are as follows:

- For binary plants at reservoirs in the temperature range of 150° to 200°C, reduce typical cost of power by 8 to 20 percent through improvements in efficiency and in O&M cost components in the mid-term.

- For flash plants, reduce typical cost of power by 2 to 6 percent through improvements in materials and auxiliary equipment related to scaling, corrosion, and other brine-handling requirements in the mid-term.

The Level II Objective for the Hard Rock Penetration Task is to reduce the life-cycle cost of hydrothermal electricity by 10 to 13 percent through improvements in fluid production and procedures in the mid-term.

2.3 Project: Materials Development

Level III Objectives of the Conversion Technology and Hard Rock Penetration Tasks being addressed by the Materials Development Project are as follows:

- Reduce costs associated with lost circulation episodes by 30 percent in the near-term.

- Reduce costs of deep wells and directionally drilled wells by 10 percent in the near-term.

- Reduce well cementing problems for typical hydrothermal wells by 20 percent in the near-term.

- Reduce the cost of binary power cycles by the development of a corrosion-resistant and low-fouling heat exchanger tube material costing no more than three times the cost of carbon steel in the near-term.

- Reduce the cost of mitigating HCl-induced corrosion in wells and steam collection piping at the Geysers by the development of low-cost composite liner systems in the near-term.

2.4 Activities: The Materials Development Project is presently comprised of the five activities listed below. Expected accomplishments as documented in the FY 1990 Annual Operating Plan (AOP) or subsequently added, are also summarized.

2.4.1 Advanced High Temperature Lightweight Cements

- Identify best candidate cement

- Complete pumpability tests

- Perform long-term durability testing in autoclaves

- o Commence downhole testing

- o Peer-review publication

2.4.2 Thermally Conductive Polymer Cement Liners

- o Issue interim report for heat exchanger test No. 1

- o Selection of modified surface formulation

- o Complete autoclave evaluation of surface-modified formulation

- o Initiate and complete field testing of heat exchanger No. 2

2.4.3 Chemical Systems for Lost Circulation Control

- o Selection of material

- o Complete mud displacement tests

2.4.4 Corrosion Mitigation at the Geysers

- o Plan cost-shared test program with steam producers

- o Complete preliminary tests to establish technical feasibility

2.4.5 Geothermal Drilling Organization Elastomer Activities

- o Liaison activities with GDO/SNL selected contractors

Without the successful completion of the above activities and others outlined in the FY 1991 AOP, the Level III Objectives for the Materials Development Project, and consequently the Level II Objectives for both the Conversion Technology and Hard Rock Penetration Tasks, will probably not be met. Advanced materials of construction represent the common denominator for all of these goals. For example, to reduce the cost of fluid production, a significant reduction in well drilling cost must be attained. To meet this goal, improved elastomers and methods for bonding them to reinforcing steel substrates are essential for use in tools such as drillpipe protectors, rotating head seals, blow-out-preventors and downhole drill motors.

Currently, the cost of correcting lost circulation problems occurring during well drilling and completion operations constitutes 20 to 30 percent of the cost of a well. One way to appreciably reduce this cost is to develop high temperature fast setting chemical systems which can be injected into the formation to seal the fissures without the necessity of removing the drillstring.

The development of lightweight CO_2-resistant well cements will reduce the frequency of lost circulation episodes during well completion operations and will extend well life when CO_2-rich aquifers are encountered.

Reductions in the corrosion rates and fouling coefficients in binary and flash plants will greatly improve the efficiency of these processes and help meet the Level II Objectives in the Conversion Technology Task. The use of thermally conductive and corrosion resistant polymer concrete liners, chemically modified to make them resistive to scale deposition, will increase the size of the hydrothermal resource that can be exploited by binary technology, and will result in reductions in the quantities of potentially toxic sludges that must be disposed of since flashing of the brine will not take place.

3. Fiscal Year Accomplishments

3.1 Task: Conversion Technology

3.2 Project: Materials Development

3.3 Activity 1: Advanced High Temperature Lightweight Cements

In order to meet the GD Programmatic Objectives of reducing well cementing problems for typical hydrothermal wells by 20 percent, improved well cements must be developed. The R&D strategy seeks to improve the effectiveness of geothermal well completion procedures and to reduce the occurrence of lost circulation problems by the development of CO_2-resistant lightweight high temperature cements. These improvements will help to transfer well-life limitations from materials to reservoir constraints in a cost effective manner. The work is being performed as a cooperative research effort with the New Zealand Department of Scientific Research (DSIR). BNL develops the cement formulations and performs physical, chemical and mechanical evaluations. DSIR is conducting downhole tests in wells at their Mokai and Rotokowa geothermal fields.

During FY 1990, work to formulate and test lightweight CO_2-resistant cements continued. In addition to resistance to CO_2 attack at high temperature, other property criteria are as follows: slurry density < 10 lb/gal, pumpable for a minimum of 4 hr at 150°C, compressive strength > 1000 psi at an age of 24 hr, water permeability < 0.1 m Darcy, and a bulk density < 62.4 lb/ft^3.

The results from the laboratory studies performed during the year first confirmed that all calcium silicate hydrate-based well cements undergo carbonation reactions when exposed to hydrothermal fluids containing CO_2. The carbonation rates are strongly dependent on CO_2 concentration, temperature and pressure. The presence of sodium cations in the fluid was found to result in alkali metal - catalyzed hydrolysis of the cement hydrates, thereby increasing the carbonation and subsequent deterioration rate.

The most promising CO_2-resistant formulation identified at BNL is a phosphate modified calcium aluminate cement. The cements yield compressive strengths far in excess of the criterion. For example, curing in air for

24 hr produces a strength of 4000 psi. Curing in hydrothermal environments at 150°C and 200°C for 20 hr yields strengths of 4740 and 10500 psi, respectively.

The formulation can meet API pumpability standards by the incorporation of conventional organic-type retarders such as gluconic acid or glucuronic-6,3 lactone. Unfortunately, these retarding materials undergo reactions with CO_2 leading to carbonation. Inorganic acid-type additives such as boric acid and sodium tetraborate decahydrate are not as effective in retarding the curing rate, but they are not susceptible to carbonation. Studies to explore other methods for extending the pumpability are planned for FY 1991.

The cost-shared cooperative program with the Department of Scientific and Industrial Research (DSIR) in New Zealand is continuing. Series of calcium aluminate cements were sent to DSIR who installed them in a well where they are being exposed to CO_2-containing brine at 320°C and pH ~2.2. After only 3 months in this environment, conventional well cements had volume reductions of up to 20% and were completely carbonated. To date, none of the BNL-supplied samples have been removed for evaluation.

The results from the FY 1990 studies can be summarized as follows:

1. Phosphate-bonded calcium aluminate cement showed great promise as a CO_2-resistant binder.

2. Calcium aluminate cements are not pumpable without the addition of retarders.

3. Conventional organic-type retarders yield pumpable slurries but are susceptible to carbonation.

4. Inorganic acid additives (boric acid, borax) are not as effective retarders, but they are not subject to carbonation.

5. Initial data from downhole testing at DSIR received.

Planned FY 1990 milestones for this activity are listed in Section 2.4.1. Milestones 1, 4 and 5 were completed, one set of autoclave exposures (Milestone 3) was completed and another is in progress. Pumpability testing (Milestone 2) was initiated and is an ongoing effort during the evaluation of retarding admixtures.

During FY 1990, spending for this activity amounted to $155K. A total of 1.4 man-years of scientific and professional labor was committed to the work. The work on lightweight CO_2-resistant cements for 300°C hydrothermal well completions is on schedule and the technology transfer process to industry should be completed by the end of FY 1992.

Activity 2: Thermally Conductive Polymer Cement Liners

One of the Level III Goals of the Conversion Technology Task is to reduce the cost of binary power cycles by development of low cost corrosion and scale resistant materials of construction for heat exchanger tubing. This activity investigates the use of thermally conductive composites for this application.

Corrosion of the brine side of tubing in shell and tube heat exchangers can be a major problem in binary plants unless a very expensive high alloy steel (AL-29-4C) is used. Even then, excessive fouling prevents the economic use of binary processes with hypersaline brine reservoirs. Both problems could possibly be solved with the development of thermally conductive corrosion and scale resistant polymer concrete liners for steel tubing. The work consists of determinations of the effects of composition and processing variables on the thermal and scale-resistance characteristics of the composite, and measurements of the physical and mechanical properties after exposure to hot brine under laboratory and field conditions.

Referring to the list of planned milestones for FY 1990 given in Section 2.4.2, only milestones 2 and 3 were attained. Milestones 1 and 4 required the selection of a field test site and award of a contact by DOE/IDO to the commercial operator of that site (Red Hill Geothermal, Inc.). Both were completed late in FY 1990, but start-up of the field testing of the prototype shell and tube heat exchanger containing 80 ft of lined tubing was delayed until early FY 1991. The unit was assembled and installed at the site by INEL. The fluid to be used in the test is at a temperature of 183°C, and has a salt content of ~275,000 ppm. Under heat exchange operations, its scaling and silica deposition rate is 5 in./yr.

Prior to assembly at the Red Hill Geothermal site, INEL performed "base line" testing at the Geothermal Test Facility (GTF). A non-scaling brine was used in this test in order to obtain heat transfer and fluid flow information for a clean tube. The results from these tests which were performed at an inlet temperature of 170°C indicate that compared to a AL-29-4C tube, the polymer cement lined tubing had a lower heat transfer coefficient and a higher pressure drop. Both characteristics would be expected to improve when industrial-scale fabrication methods are utilized. The FY 1990 budget for this activity was $85K. A total of 0.72 man years of scientific, professional and technical staff time was committed to the activity. Completion of this activity by the end of FY 1991 is scheduled.

Activity 3: Chemical Systems for Lost Circulation Control

Currently, the cost of correcting lost circulation problems occurring during well drilling and completion operations constitutes 20 to 30 percent of the cost of a well. The GD Level III Objective is to reduce well drilling costs for typical hydrothermal wells by 10 percent in the near term. A significant cost reduction can be accrued if an advanced high temperature chemical system that can be introduced through the drill pipe into the lost circulation zones is developed. Elimination of the need to remove the drill string will not only greatly reduce down time, but it will also aid in the location of fractured zones.

During FY 1990, R&D work was continued as a cooperative effort with Sandia National Laboratories (SNL). Experiments were performed with a previously identified bentonite-ammonium polyphosphate-borax-magnesium oxide system to determine methods for controlling the curing rates and, therefore, pumpability. Microencapsulation of the magnesium oxide in organics was determined to be an effective method for controlling pumpability. The formulations were then optimized with respect to placement and formation temperatures and the resultant mechanical properties of the cured cements.

Six potential methods for placement of the advanced chemical systems into fractured zones were identified by SNL. These are listed below: (1) pumped through open drill pipe, (2) pumped through drillable straddle packer, (3) pumped through bit using encapsulated accelerator, (4) pumped through bit using downhole injector, (5) pumped through wireline-deployed porous poker, and (6) pumped through drillstring - deployed porous poker. For each of these methods the pumpability requirements, material quantities, setting times, and operating temperatures were estimated and these needs were then matched with the laboratory identified materials characteristics. Advanced high temperature rapid setting materials suitable for placement using methods 1 and 2 appeared to be available today, and they will be tested on a larger scale by SNL in prototype placement equipment in FY 1991. Materials for use with methods 3-5 require additional optimization in FY 1991, but should be ready for prototype testing in FY 1992, in time to meet the Level III Objective.

Planned FY 1990 milestones for this activity are listed in Section 2.4.3. Milestone No. 1 was completed although work to optimize the formulation for use with the six potential placement techniques listed above is continuing. Mud displacement tests (milestone No. 2) were performed in small-scale laboratory equipment, and larger scale testing will be performed in conjunction with SNL in FY 1991.

The FY 1990 budget for this activity was $95K. A total of 0.86 man-years of scientific, professional and technical staff time was committed to the activity.

Completion of the activity is scheduled for FY 1992. However, depending upon the nature and extent of any lost circulation problems encountered during the Phase 2 drilling of the Long Valley Exploratory Well scheduled for the Summer of 1991, the advanced materials may be deployed at that time.

Activity 4: Corrosion Mitigation at the Geysers

Increased HCl concentrations in the steam produced from geothermal wells at the Geysers have resulted in severe corrosion problems in the upper regions of the well casing where some condensation occurs, and in the steam collection piping. In some cases this has resulted in the shutdown of wells causing reduced steam supply and, therefore, decreases in electric power generation. Increased operating costs and safety and environmental concerns have also resulted.

In mid FY 1990 based upon an industrial request to DOE/GD, BNL initiated cost-shared work with the Coldwater Creek Operator Company to determine the technical feasibility for the use of previously developed polymer cement composites for corrosion protection. Two BNL - supplied test sections were installed at the Geysers at locations where failure of 0.5 in. thick wall steel casing generally occurs within 5 weeks. Neither test section failed during a five week test, but some chemical attack was apparent. The probable cause of this attack was the presence of an excessive amount of portland cement in the formulation and the presence of a significant amount of laitance on the liner surface. Normally, the hydrothermal stability of polymer cements is improved by the addition of insoluble forms of calcium-containing compounds found in portland cement, but acid resistance is decreased. Therefore, for use in a high temperature (170° to 200°C) highly acidic (pH 2-4) environment, an optimization of the formulation with respect to fluid temperature and pH is required. This study is scheduled to be made early in FY 1991 and it will be followed by the field testing of coated test coupons and lined 8-in. diameter x 12-in. long wellhead sections.

In addition to the Coldwater Creek Operator Company, Unocal and the Northern California Power Authority indicated a desire to participate in this program, the results from which should help to mitigate corrosion, thereby making the use of many marginal production wells cost effective while enhancing safety.

The FY 1990 budget for this activity was $60K. A total of 0.72 man-years of scientific, professional and technical staff time was committed to the activity.

Contingent upon the results from the work described above, several 10 to 12-ft lengths of 16-in.-diam. well casing will be lined and installed at the top portion of Coldwater Creek wells. A completion date of July 1991 for this work is expected. The work will then be expanded to include the installation of lined casing to depths of several hundred feet by the end of FY 1991.

Activity 5: <u>Geothermal Drilling Organization Elastomer Activities</u>

BNL provides liaison services to SNL and the Geothermal Drilling Organization (GDO) in order to enhance the transfer of completed GD-sponsored high temperature elastomer technology to industry so that it can be utilized in equipment needed by the GDO. Such needs include drillpipe protectors, rotary head seals, blow-out protectors, and Moineau stators for downhole drillmotors.

Work on the development of advanced high temperature drillpipe protectors was essentially completed by the GDO selected contractor, Regal International. Based upon laboratory and field testing conducted in FY 1989, and a FY 1990 field test, it was concluded that the unavailability of a hydrothermally stable chemical coupling system needed to bond the elastomers to steel reinforcement, prevented the development of a tool which met the GDO requirements. However, the program increased the operating capability for oil and gas applications, and the tool is being commercialized for those uses.

Development of advanced rotary head seals was continued by A-Z Grant International under contract with GDO. Two promising elastomers and a bonding system were identified and laboratory tested, a sealing configuration designed, and full-scale seal units fabricated. Field testing will commence in FY 1991.

Funding ($8K) to cover the BNL liaison activities was provided by SNL. A total of 0.07 man-years of scientific manpower was committed to the activity. Both projects will be completed in FY 1991, but it should be noted that the lack of a suitable bonding agent will prevent the successful development of an advanced drillpipe protector. Starting in FY 1991, the Materials Development Project will address this need.

4. Management

4.1 Organization

The technical and administrative management of the R&D phases of this project are under the direction of BNL with project policy established by the GD Task Manager, Raymond LaSala.

Fiscal control by BNL is exercised in the form of monthly comparisons, over the project term, of actual costs incurred against corresponding line items of the budget. Technical results are monitored through a periodic review, by the Contractor Project Manager, of accomplishments by measuring actual performance with generally accepted standards for R&D and other investigative or analytic procedures, as observed by universities and large independent research facilities including BNL.

4.2 Management Structure

The GD Manager of the Geothermal Materials Project is Raymond LaSala (FTS 896-4198). Field level program monitoring is provided by Ken Taylor of the Idaho Falls Operations Office (FTS 583-9063). Field level management is by the Contractor Work Proposal Managers at BNL, Leon Petrakis, Chairman, Department of Applied Science (FTS 666-3037) and John Andrews, Head, Energy Efficiency and Conservation Division (FTS 666 7726). The Principal Investigator at BNL is Lawrence E. Kukacka, Leader, Process Materials Group (FTS 666-3065).

4.3 Work Breakdown Structure

Task Management: R. LaSala, DOE-HQ
Project Management: K. Taylor DOE-IDO
Principal Investigator: L.E. Kukacka, BNL

- Cements: T. Sugama
- Thermally Conductive Composites: T. Sugama, L. E. Kukacka
- Lost Circulation Control: R. Webster
- Corrosion Mitigation: R. Webster
- Elastomers: L. E. Kukacka

4.4 Interfaces/Contacts

National Laboratories
Conversion Technology Task, G. Mines, INEL
Hard Rock Penetration, J. Dunn, SNL

Geothermal Drilling Organization

J. Dunn, SNL
R. Wemple, SNL
S. Pye, Unocal
J. Combs, Geothermal Resources Int.
T. Bailey, A-Z Grant/Drilex
T. Thomerson, Regal International

Geysers Support

D. Prideau, Coldwater Creek Operator Co.
S. Enedy, NCPA
T. MacPhee, Unocal
W. C. Allen, Unocal

4.5 Meetings/Reviews

Hard Rock Penetration Task Industrial Review Panel, February 7-8, 1990, San Diego, CA.

Program Review at DOE/GD-HQ, February 1990
DOE Geothermal Program Review VIII, April 1990, San Francisco, CA

4.6 Issues

None

5. Reports

The following technical documents were issued during FY 1990:

Sugama, T., Kukacka, L. S. and Carciello, N. Cement hydrate catalyzed hydrolysis of polyimide lightweight materials. BNL 43270, Jan. 1989; J. App. Poly. Sci., 40, 1857-70 (1990).

Kukacka, L. E. Advanced materials for geothermal applications. Proc. DOE Geothermal Program Review VIII, San Francisco, April 1990, pp 35-40, DOE Conf-9004131, Washington, DC, 1990.

Sugama, T., Gray, G., and Carciello, N. R. Influences of set-retarding admixtures on alkali carbonation of calcium aluminate cements under hydrothermal conditions. J. Mat. Sci. and Tech., in press.

Sugama, T., and Carciello, N. R. The development of strength in phosphate bonded calcium aluminate cements. J. Am. Ceramics Soc., in press.

Sugama, T., Gray, G., and Carciello, N. R. The interface between zinc phosphate-deposited steel fibers and cement paste. BNL 44759, July 1990; J. Mat. Sci., in press.

Kukacka, L. E. Geothermal materials development, annual report FY 1989.

Kukacka, L. E. Geothermal materials project input for conversion technology task, annual operating plan FY 1991, August 1990.