

BNL--41162

DE88 012135

DECREASING GEOTHERMAL ENERGY CONVERSION COSTS
WITH ADVANCED MATERIALS

Lawrence E. Kukacka

March 1988

Prepared presentation at the
Sixth Annual Department of Energy
Geothermal Program Review
April 19-21, 1988
San Francisco, CA

Process Sciences Division
Department of Applied Science
Brookhaven National Laboratory
Associated Universities, Inc.

This work was performed under the auspices of the Department of Energy,
Washington, DC under contract No. DE-AC02-76CH00016

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DECREASING ENERGY CONVERSION COSTS WITH ADVANCED MATERIALS

Lawrence E. Kukacka
Process Sciences Division
Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

ABSTRACT

If the Geothermal Technology Division (GTD) is to meet its programmatic objectives in hydrothermal fluid production and energy conversion, it is essential that new materials of construction be available. Level III Program Objectives include 1) reducing the costs associated with lost circulation episodes by 30 percent by 1992, 2) reducing the costs of deep wells and directionally drilled wells by 10 percent by 1992, 3) reducing well-cementing problems for typical hydrothermal wells by 20 percent by 1991, and 4) the development of a corrosion-resistant and low-fouling heat exchanger tube material costing no more than three times the cost of carbon steel tubes by 1991.

The Brookhaven National Laboratory (BNL) materials program is focused on meeting these objectives. Currently, work is in progress on 1) high temperature chemical systems for lost circulation control, 2) advanced high temperature (300°C), lightweight (~1.1 g/cc), CO₂-resistant well cementing materials, 3) thermally conductive composites for heat exchanger tubing, and 4) ultra high temperature (600°C) cements for magma wells. In addition, high temperature elastomer technology developed earlier in the program is being transferred for use in the Geothermal Drilling Organization programs on drill pipe protectors, rotating head seals, and blow-out preventors. Recent accomplishments and the current status of work in each subtask are summarized in the paper.

INTRODUCTION

In order to meet GTD's Programmatic Objectives, attainment of which will greatly enhance development of the Nation's geothermal resources, advanced technology is required for industry to reduce costs caused by the severe geothermal environments encountered during drilling, well completion and test field development, heat extraction, power production, and reinjection of spent

brine. Particular needs are for improved materials and methods to withstand 1) extremely high temperatures encountered in geothermal reservoirs and in energy conversion processes, and 2) severe corrosion and scaling by geothermal brines. Materials needs exist for specific components such as downhole drill motors, pumps, casing, packers, blow-out preventors, drill-pipe protectors, rotating head seals, and heat exchangers. In particular, improvements in lost-circulation control, lightweight well-completion materials, and downhole drill motors would significantly reduce well costs.(1)

The GTD initiated the Geothermal Materials Program in 1976, and since 1978, BNL has provided technical and managerial assistance in the implementation of this long-term high-risk effort.

To date, the most significant geothermal materials advance has been in high temperature elastomers. Developed under GTD sponsorship by L'Garde, Inc., the Y-267 EPDM (ethylene, propylene, diene, methylene) elastomer can be classified as a technology breakthrough.(2,3) Three major U.S. seal manufacturers acquired the technology from the Department of Energy (DOE) in 1982, and molded parts are now commercially available from these and other firms. The elastomers are widely used in well logging tools, packers, valves and other equipment. Recently, GTD-sponsored work has been performed to modify the Y-267 EPDM to enhance its performance in drill pipe protectors, rotating head seals, and blow-out preventors, and these results are being utilized in the Geothermal Drilling Organization's programs on these components.

Another successful materials advance was the development of high-temperature polymer concrete formulations. These materials are now available for use as corrosion resistant linings at temperatures up to 260°C.(4)

Cements represent another area where considerable progress has been made. The results from this effort currently serve as the basis for the selection of cements used for geothermal well completions throughout the world.(5) There is still, however, a major need for improved lightweight CO₂-resistant cements.(6,7)

Handbooks summarizing the performance of materials in above-ground and downhole geothermal environments are other widely used outputs from the materials program.(8,9)

Research and development (R&D) efforts aimed at further cost reductions, in accordance with GTD Programmatic Objectives, are currently in progress. Tasks include work on high temperature lightweight cements, chemical systems for lost circulation control, nonmetallic heat exchanger tubing, and ultra high temperature cements. R&D on elastomers for dynamic sealing applications and for liners on well casing was discontinued at the end of FY 1987, but technology transfer efforts on these materials are continuing. Major accomplishments during FY 1987 and the thrust of the current efforts are summarized below.

1. High Temperature Cements

- Surface treatment of sillimanite-based microspheres for strength and durability enhancement of lightweight cements.
- Oxidation of carbon fiber surfaces for bond enhancement in lightweight cements.
- Downhole characterization of lightweight cements at ~300°C in low CO₂-containing brines.

2. Chemical Systems for Lost Circulation Control

- Optimization of previously identified systems.
- Microencapsulation of reactive components.
- Engineering-scale placement tests.

3. Materials for Nonmetallic Heat Exchangers

- Fabrication of prototype heat exchanger tubing.
- Laboratory durability tests.
- Field measurements of fouling coefficients and corrosion rate.

4. Ultra High Temperature Cements

- Identification of pumpable ceramic-type materials stable at $>500^{\circ}\text{C}$.

5. High Temperature Elastomers for Dynamic Sealing Applications

- Completed modifications of Y-267 EPDM to optimize for dynamic seals.
- Identified high temperature chemical coupling system for bonding Y-267 EPDM to carbon steel.
- Liaison with Geothermal Drilling Organization on full-scale test of drill pipe protectors.

Detailed descriptions of each of these tasks are given below.

RESULTS

1. Advanced High Temperature Lightweight Cements

In order to meet the GTD Programmatic Objectives of reducing well cementing problems for typical hydrothermal wells by 20 percent by 1991, 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 conducts the downhole tests in wells at their Mokai and Rotokawa geothermal fields.

Two very promising lightweight cements were developed, and they are currently being tested downhole by DSIR. This test is being conducted in a low CO₂-containing brine at ~310°C. Tests in fluids containing higher CO₂ concentrations are planned for next year. One formulation consists of class H cement, silica flour, water, a sodium alpha olefin sulfate foam generator, and carbon fiber.⁽¹⁰⁾ The material has a slurry density of 1.2 g/cc, a bulk density of ~1.0 g/cc, and a 24 hr compressive strength of 1200 psi. Recent data indicate that oxidation of the carbon-fiber surfaces prior to mixing results in significant enhancement of the fiber-cement interfacial bond, thereby giving further improvements in strength and durability.⁽¹¹⁾

The second promising cement formulation contains class H cement, silica flour, water, and calcium hydroxide [Ca(OH)₂]-treated ceramic microspheres. This formulation has a slurry density of 1.19 g/cc, a bulk density of 0.91 g/cc, and a 24 hr compressive strength of 1400 psi.⁽¹²⁾ Pretreatment of the sillimanite [Al(AlSiO₅)]-containing microspheres with deionized water and Ca(OH)₂ at 200°C is essential for producing a high quality cement that will meet the American Petroleum Institute's (API) criteria for geothermal cements. Specimens prepared without the pretreated spheres exhibited a compressive strength of 610 psi and a water permeability of 7.9×10^{-4} darcy after curing for 24 hr in a 300°C hydrothermal environment. API criteria are >1000 psi and <10⁻⁴ darcy, respectively. The advanced BNL cement yielded values of 1440 psi and 5.6×10^{-6} darcy. After a 180 day exposure to 300°C brine, the samples still met the API criteria.

Currently, work to develop lightweight CO₂-resistant cements is in progress. Emphasis is being placed on calcium aluminate-based materials. Laboratory evaluations are to be completed by the end of FY 1988, at which time downhole testing at DSIR will commence.

2. 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 GTD Objective is to reduce well drilling costs for typical hydrothermal wells by 10 percent by 1991. Therefore, our goal is to

develop an advanced high temperature chemical system that can be introduced through the drill pipe into the lost circulation zones. Elimination of the need to remove the drill string will greatly reduce down time and aid in the location of the fractured zone, resulting in considerable cost savings.

During FY 1984 and 1985, BNL developed two promising chemical formulations, but due to budget constraints, the task was suspended.(13,14) Work was resumed in FY 1988.

One formulation is composed of bentonite, ammonium polyphosphate (AmPP), borax, magnesium oxide, and water. The appropriate combination of these ingredients results in the formation of slurries with viscosities and thickening times adequate to allow placement. After curing at elevated hydrothermal temperatures, the cement produced was characterized by a compressive strength >500 psi at 2 hr age, a permeability to water $<2.0 \times 10^{-4}$ darcy, and a linear expansion >15 percent. Consistometer tests performed at Sandia confirmed the pumpability of the materials at high temperature and pressure.

The second promising system consists of cement, borax, glass fiber, and bentonite. The system is pumpable at 250°C, and at 2 hr age has a compressive strength of 400 psi, a water permeability of 2×10^{-3} darcy, and a linear expansion of ~2 percent.

In FY 1988 emphasis is being placed on the bentonite-AmPP-borax-magnesium oxide (MgO) system. Since the pumpability and curing times for the system can be closely controlled over a wide temperature range (150°-350°C) by varying the MgO concentration, methods for the microencapsulation of it in plastics are being investigated. As conceived, these MgO-containing capsules will be mixed with the other constituents and pumped down the drill pipe. Depending upon the thickness and thermal stability of the encapsulant, the combination of temperature and shear forces at the nozzle will be sufficient to rupture the capsule, thereby mixing the highly reactive MgO with the other materials. Curing will take place within seconds.

The laboratory phase of the task will be completed by December 1988, at which time plans will be made for a mud displacement test as a cooperative effort with Sandia National Laboratories and industry. Contingent upon these results, a well demonstration could be conducted early in 1990.

3. Materials for Nonmetallic Heat Exchangers

One of the objectives of GTD's Energy Conversion program is to improve the net geothermal fluid effectiveness of binary plants. Based upon the results from a recent Idaho National Engineering Laboratory study,⁽¹⁵⁾ the development of a low cost corrosion and fouling resistant heat exchanger tube which could be used as a substitute for high alloy tubes, could reduce the generating cost of electricity up to 10 percent. Therefore, the goal of this task is to develop a corrosion-resistant and low-fouling heat exchanger tube material costing no more than three times the cost of carbon steel tubes by 1991.

During FY 1987, a polymer concrete formulation consisting of 9 weight percent styrene, 6 weight percent trimethylolpropane trimethacrylate, and 85 weight percent silicon carbide was selected as a thermally conductive, corrosion resistant, and potentially low-fouling liner material.⁽¹⁶⁾ Autoclave exposure tests of lined tubes in brine at 150°C were initiated, and to date after 120 days, deterioration or scaling have not been detected. Centrifugal casting techniques for applying the liner onto tubes varying in size from 0.375 to 1.0 in. were also developed. Preliminary cost estimates indicated that the cost of the lined tubing will only be ~50 percent greater than that of carbon steel, well below the GTD criterion.

Currently, work is in progress to field test a prototype 80-ft long single tube shell and tube countercurrent heat exchanger as a cooperative effort with INEL. The tube diameter will be 0.75 in. and water will be the shell-side fluid. This test is scheduled to start in October 1988. The test site is currently being selected. Contingent upon the results from this test, a prototype multi-tube brine/organic heat exchanger will be fabricated and tested.

4. Ultra High Temperature Cements

This is a new project initiated in FY 1988 with the goal of designing and developing ceramictype cementitious materials systems that can be used for the completion of wells in magma environments. It is also expected that since all of the materials to be considered will not be vulnerable to carbonation, their use with the lightweight aggregates discussed in Task 1 should result in excellent lightweight CO₂-resistant cements for hydrothermal wells. For the magma application, the cement must be capable of withstanding corrosive fluids and gases in rhyolite magma environments at depths from 3 to 8 Km, pressures from 7,000 to 30,000 psi and temperatures up to 850°C. Specific criteria that the material must meet are as follows:

1. 24-hr compressive strength 10,000 psi.
2. Stability in volatile components (H₂O, CO₂, S, Cl and F) and in fusing rhyolite glasses at 850°C.
3. Cement/superalloy bond strength >10 psi.
4. Non-corrosive to superalloy casing.
5. Maintenance of pumpability at temperatures up to 300°C for 4 hr.

The scope of the work in FY 1988 is to select and evaluate various ceramic composites consisting of a matrix and a filler prepared at temperatures of up to 1000°C and atmospheric pressure. During the placement of material in the magma zone, the chemical structure of cements appears to transform from a hydrogen bond-based slurry to a hydraulic bond-based product, and then to a ceramic bond. Thus, it is important to note that possible strength retrogression during this phase transformation is an important factor to be considered in the evaluation of potential material systems.

To date, screening experiments on several systems have been performed. On the basis of these preliminary laboratory experiments, five promising binder systems were selected: Al₂O₃-TiO₂-CaO-H₂O, Al₂O₃-TiO₂-Amorphous Al Hydroxide gel (called solid-gel reaction), Al₂O₃-TiO₂-Amorphous Ti Hydroxide gel, Al₂O₃-TiO₂-Amorphous Zr Hydroxide gel, and MgO-Polyphosphate-NaB₄O₇·10H₂O-H₂O. Tests to measure the mechanical and physical properties under dry and hydrothermal conditions at temperatures of up to 1000°C are currently being made.

5. High Temperature Elastomers for Dynamic Sealing Applications

This project which was completed in FY 1987, consisted of applied research to optimize the Y-267 EPDM elastomer formulation, developed earlier by GTD for static seal applications, for use in dynamic seal applications at temperatures up to 260°C. Elastomers for these conditions do not currently exist, and a successful development and subsequent utilization in downhole drill motors, drill pipe protectors, rotating head seals, and blow-out preventors could substantially reduce drilling and completion costs to meet GTD Objectives by 1992.

During FY 1987, a series of screening tests on 15 developmental compounds were completed and the results compared with those from the base case Y-267 EPDM. Based upon these results, one was selected for a final life expectancy test. The composition and properties of this formulation are compared with those of the Y-267 EPDM in Tables 1 and 2, respectively.

**TABLE 1. DYNAMIC SEALS
MOST PROMISING FORMULATION**

<u>Constituent</u>	<u>Control Y-267</u>	<u>Formulation 485</u>
Nordel 1660	100	100
Hypalon 20	5	5
Polybutadiene 6081	20	20
Thermoguard S	5	5
N110 Black	75	50
Cyanox 2246 ^a	0.5	0.5
Dicup R ^b	3.5	3.5

a, antioxidant

b, peroxide curing agent

TABLE 2. DYNAMIC SEALS
PHYSICAL PROPERTIES

<u>Property</u>	<u>Control Y-267</u>	<u>Formulation 485</u>
Tensile, psi	1973	2190
Elongation, %	122	137
Die B, ppi	169	—
Die C, ppi	223	226
Set, %	5.3	—
Shore Hardness at 20°C	92	85
Life Test in DSST, hr	8	>49 ^a

^a, test voluntarily terminated before any sign of failure.

A life expectancy test was performed on Compound 485 and the Y-267. Test conditions were as follows: brine temperature 204°C, shaft speed 350 rpm, and pressure gradient 300 psi. After 8 hr in test, the Y-267 failed. In comparison, testing of Compound 485 was voluntarily terminated after 49 hr. Visual examination of the seal indicated some deterioration, but at shutdown it was still performing well. The cause of the Y-267 EPDM failure was not apparent. The post-test physical and mechanical properties of both sealing materials were measured, and they will be included in the final report which should be published by July.

BNL has initiated liaison responsibilities with Sandia National Laboratories and the GDO on their program on elastomers for drill pipe protectors, rotating head seals and blow-out preventors. A contract for the drill pipe protectors has been placed by Sandia with Regal International, Inc., and work started in December 1987. The specified design conditions for this application are as follows:

1. Brine containing 180,000 ppm TDS and 10 atm CO₂ at 288°C and 5000 psi.
2. Steam at 600 psi and 260°C.
3. In both environments, a side load of 3500 lb during rotation must be tolerated.

All of the GTD-sponsored data on high temperature elastomers for dynamic seals and chemical coupling systems for bonding them to metal substrates will be utilized in the GDO effort.

CONCLUSIONS

The DOE Geothermal Materials Program is addressing problems whose solutions have a short to moderate term impact on the operation of plants as well as conducting long-term R&D designed to have significant impacts on industrial viability and productivity in materials performance. Active technology transfer linkages are established and maintained. To date, the program has resulted in the development of the best known high temperature elastomer for geothermal service, and several other outputs from the program and are being used or tested by industry. Current efforts on dynamic seals and lightweight well cements may be used by industry in the very near future. Other efforts on CO₂-resistant cements, lost circulation control materials, and nonmetallic heat exchanger tubing will require longer development times, but should meet scheduled GTD Objectives.

REFERENCES

1. "Geothermal Energy Technology, Issues, R&D Needs, and Cooperative Arrangements," National Research Council, National Academy Press, Washington, D.C., 1987.
2. Hirasuna, A. R., et al., A Proven Elastomer Compound for Extremely Hostile Geothermal and Oilfield Environments, IADC/SPE Drilling Conference, Paper 11407, New Orleans, February 1983.
3. Hirasuna, A. R., et al., Elastomer Liners for Geothermal Tubulars, Y-267 EPDM Liner Program, BNL 40946, December 1987.
4. Kaeding, A. O., Design and Fabrication of Polymer-Concrete-Lined Pipe for Testing in Geothermal Energy Processes, Final Report. BNL 33019, July 1981.
5. "API Work Group Reports Field Tests of Geothermal Cements," Oil and Gas Journal 94, 93-97, February 11, 1985.
6. Milestone, N. B., Sugama, T., Kukacka, L. E., and Carciello, N., Carbonation of Geothermal Grouts - Part 2: CO₂ Attack at 250°C. Cem. and Conc. Research, 17, 37-46 (1987).
7. Milestone, N. B., Sugama, T., Kukacka, L. E., and Carciello, N., Carbonation of Geothermal Grouts - Part 3: CO₂ Attack on Grouts Containing Bentonite. Cem. and Conc. Research, 17, 37-46 (1987).

8. Ellis, P. F., et al., Materials Selection Guidelines for Geothermal Energy Utilization Systems, DOE/RA/2726-1, January 1981.
9. Ellis, P. F., et al., Corrosion Reference for Geothermal Downhole Materials Selection, DOE/SF/11503-1 (DE 83010306), March 1983.
10. Sugama, T., Kukacka, L. E., and Galen, B. G., Advanced High-Temperature Lightweight Foamed Cements for Geothermal Well Completions, BNL 38087, April 1986. Proc. Geothermal Resources Council 1986 Annual Meeting, Palm Springs, CA, September 1986.
11. Sugama, T., Kukacka, L. E., Carciello, No., and Galen, B., Oxidation of Carbon Fiber Surfaces for Improvement in Fiber-Cement Interfacial Bond at Hydrothermal Temperature of 300°C. Cem. and Conc. Research, (in press).
12. Sugama, T., Kukacka, L. E., Treated Ceramic Microsphere-Cement Lightweight Composites for Geothermal Cementing Systems, Proc. Geothermal Resources Council 1987 Annual Meeting, Sparks, NV, Vol II, 75-80, October 1987.
13. Sugama, T., Kukacka, L. E., Warren, J. B., and Galen, B. G., Bentonite-Based Ammonium Polyphosphate Cementitious Lost-Circulation Materials, J. Mat. Sci., 21, 2159-2188 (1986).
14. Sugama, T., Kukacka, L. E., Galen, B. G., and Milestone, N. B., Characteristics of High Temperature Cementitious Lost-Circulation Control Materials for Geothermal Wells, J. Mat. Sci., 22, 63-75 (1987).
15. Bliem, C. J., and Demuth, O. J., Value Analysis for the Use of Polymer Concrete-Lined Heat Exchanger Tubes in Binary Geothermal Power Plants, draft unpublished report, INEL, February 1988.
16. Fontana, J. J., Reams, W., and Cheng, H. C., Potential Polymer Concrete Heat Exchanger Tubes for Corrosive Environments, Proc. International Congress in Polymers in Concrete, Brighton Polytechnic, Brighton, UK., 399-403, September 1987.