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ADVANCED MATERIALS FOR GEOTHERMAL ENERGY PROCESSES

Lawrence E. Kukacka

August 1985

Prepared for presentation at the
Fourth Annual DOE Geothermal Program Review
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September 11-12, 1985

PROCESS SCIENCES DIVISION

DEPARTMENT OF APPLIED SCIENCE

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Abstract

Advanced Materials for Geothermal Energy Processes

The primary goal of the geothermal materials program is to ensure that the private sector development of geothermal energy resources is not constrained by the availability of technologically and economically viable materials of construction. This requires the performance of long-term high risk GHTD-sponsored materials R and D. Ongoing programs to be described include high temperature elastomers for dynamic sealing applications, advanced materials for lost circulation control, waste utilization and disposal, corrosion resistant elastomeric liners for well casing, and non-metallic heat exchangers.

ADVANCED MATERIALS FOR GEOTHERMAL ENERGY PROCESSES

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SUMMARY

The Geothermal Technology Division initiated the Geothermal Materials Program in 1976 to ensure that the private sector development of geothermal energy resources is not constrained by the availability of technologically and economically viable materials of construction. Since 1978 Brookhaven National Laboratory (BNL) has provided technical and managerial assistance in the implementation of the long-term high-risk effort. Major successes have been attained in the development of elastomers for high-temperature applications and in the use of polymer concrete liners for corrosion protection. Both technologies have been successfully transferred to industry.

In the case of the high temperature Y-267 EPDM (ethylene propylene, diene, methylene) elastomer, the operating limits for elastomeric parts were increased from the range 149°C-204°C to 260°C-316°C. Based upon extensive testing by L'Garde, Inc., and over 25 other organizations during the past 6 yr, no better elastomer for geothermal service is known. Reductions in cost up to several hundred times compared to those of other high temperature elastomers have been attained. Over 15 laboratory and 20 field case histories have been documented. Current uses include seals in logging tools, casing packers, gate valves, BOP rams, shock subs, and jars.

The materials program has also produced the most comprehensive and thorough examination of the geothermal cementing problem undertaken thus far. As part of the program, the first known downhole testing of cements in a flowing geothermal well was conducted. Nine cements satisfied the test criteria. Unfortunately the exposure temperature was only 214°C, and

it is considered essential to have data at a temperature of at least 300°C before definitive conclusions can be made regarding the hydrothermal stability at economically attractive well conditions. Current budget constraints prevent the performance of these needed tests.

Research and development efforts aimed at further cost reductions and extension of service life are currently in progress. Tasks include high temprature elastomers for dynamic sealing applications, advanced materials for lost circulation control, waste utilization and disposal, corrosion resistant elastomeric liners for well casing, high temperature lightweight cements, and non-metallic materials for heat exchanger applications. The major thrusts of the FY 1985 efforts are summarized below.

1. <u>High Temperature Elastomers for Dynamic Sealing Applications</u>

   - Chemical modification of previously developed and tested Y-267 EPDM 260°C static seal material for use in dynamic sealing applications.
   - Optimization of EPDM formulations for use in critical high cost applications such as in downhole drill motors and open-hole packers.

2. <u>Advanced Materials for Lost Circulation Control</u>

   - Hydrothermally stable and pumpable chemical systems are being investigated for use as lost circulation control materials in geothermal well drilling operations.

3. <u>Pitting Resistant Steels</u>

   - Studies of the mechanism whereby high corrosion resistance is obtained through alloying of stainless steels with molybdenum combined with nitrogen.

4. <u>Geothermal Waste Utilization and Disposal</u>

   - Studies of methods for utilizing waste constituents as raw materials for cementitious binders or as nonleachable fillers in composites that can be used for general construction purposes.

- Analyses of biochemical techniques for concentration and subsequent removal of heavy metals from waste.

5. Materials for Non-Metallic Heat Exchangers

   - Development of corrosion resistant metallic and silicon carbide-filled composites which have thermal conductivities in the range of stainless steels.

6. Corrosion Resistant Elastomeric Liners for Well Casing

   - Investigation of high temperature chemical coupling systems for bonding elastomeric liners to carbon steel well casing.
   - Data on corrosion resistance of Y-267 EPDM-lined carbon steel casing for comparison with those for high chrome and nickel alloys.

7. High Temperature Geothermal Well Cements

   - Characterization of promising high temperature well cements under placement and downhole environmental conditions duplicating most of the well completion variables.
   - Preliminary screening tests on lightweight cement slurries.

8. Corrosion in Binary Geothermal Systems

   - Quantitative corrosion data from laboratory and plant tests for metals presently used in binary plants and other more potentially resistive metals and nonmetals.

9. High Temperature Cathodic Protection Systems

   - Testing and characterization of high temperature electrochemical processes designed to cathodically protect the external surfaces of well casing and heat exchangers.

Recent results from several of these efforts are given in the body of this paper. It is expected that Tasks 2, 4, 5, and 7 will continue in FY 1986.

INTRODUCTION

Among the most pressing problems constraining the development and expanded use of geothermal energy resources for electric power generation is the lack of satisfactory component and system reliability. This is due to the unavailability, on a commercial scale, of cost-effective materials that can function in a wide range of geothermal environments and to the unavailability of a comprehensive body of directly relevant test data or materials selection experience. Suitable materials are needed for service in geothermal wells and in process plant equipment. For both situations, this requires materials that can withstand high-temperature, highly-corrosive, and scale-forming geothermal fluids. In addition to requiring a high degree of chemical and thermal resistance, the downhole environment places demands on the physical/mechanical properties of materials for components utilized in well drilling, completion, pumping, and logging.

In 1976, the GHTD started the Geothermal Materials Program to address materials-related problems, and since 1978 Brookhaven National Laboratory has provided technical and managerial assistance in the implementation of the effort. Major successes have been attained in the development of elastomers for hightemperature applications[1] and in the use of polymer concrete liners for corrosion protection.[2] Both technologies have been successfully transferred to industry. Other outputs from the materials program being used by the geothermal industry include the characterization of well cements after downhole exposure to flowing brine,[3] and handbooks summarizing the performance of materials in above-ground and downhole geothermal environments.[4,5]

Achievement of the program goal requires the effective management of a wide range of technological and economic problems. The GHTD/BNL approach is to optimize the benefits of materials-related R and D through the resolution of selected problems. The program strategy concentrates on developing an optimum balance between 1) problems whose solutions have a short to moderate term impact on the operation of prototype plants, and 2) long-term R and D designed to have significant impacts on industrial viability and productivity through improvements in materials performance and costs. The program strategy is to conduct projects that 1) identify materials-related needs constraining commercialization, 2) evaluate the applicability of existing materials and technology to geothermal problems, 3) develop specific and generic solutions to materials problems that have major impacts on geothermal energy costs and productivity, and 4) provide appropriate and adequate incentives and mechanisms for the stimulation of industry-sponsored geothermal materials R, D and D.

RESULTS

1. High Temperature Elastomers For Dynamic Sealing Applications

This project performs applied research to optimize a Y-267 EPDM elastomer formulation, developed earlier by GHTD 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 could substantially reduce drilling and completion costs. The effects of compositional changes on the properties of the elastomer are being determined, and the formulation optimized to yield the specific sealing requirements. Prototype and full-scale testing will be performed. Based upon the results from the generic research, a specific sealing application will be targeted for continued R and D.

The Y-267 EPDM elastomer compound was originally developed for geothermal casing packer applications.The primary requirements were to develop a thermochemically stable compound with excellent extrusion resistance. Consequently, the Y-267 EPDM compound contains no special consideration for dynamic seal applications. However, it is highly abrasion resistant, a characteristic that comes along with its excellent extrusion resistance which is partially provided by a small particle size black.

The current project is to modify the Y-267 EPDM compound for better dynamic seal characteristics while maintaining its excellent thermochemical resistance. The effort is centered around improving the lubricity and the lubricability of the compound. The effort evaluates developmental compounds in a simple rotating (300 rpm) shaft environment at 204°C with differential pressures up to 250 psi. Once the initial development is complete, the development will move into a phase devoted to a specific application, e.g., Moineau motor stator. The precise application will be selected based on the results of the initial development. The initial development is scheduled for completion towards the end of calendar year 1985.

2. Advanced Materials for Lost Circulation Control

This project is investigating hydrothermally stable and pumpable chemical systems for use as lost circulation control materials (LCM) at temperatures up to 300°C. Lost circulation problems directly and indirectly represent 20 to 30% of geothermal well costs, and high temperature materials that will yield permanent repairs that can be made without removal of the drill string in order to set casing and cement, do not exist. The investigations include laboratory studies of interactions between bentonite-based drilling muds, reactive solid additives, and chemical fluids. The pumpability characteristics of the slurries and the properties of the cured materials are also determined.

An interim report describing results through March 1985 has been published.[6] A formulation which appears to have high potential as a new cementitious lost circulation control material 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%. The reaction compound responsible for the strength development at 300°C was found to be an assemblage of interlocking crystals composed of a grown thin-plate crystal. It was inferred that this microcrystalline cluster is associated with montmorillonite and AmPP-based complex formations. Consistometer tests performed at Sandia confirmed the pumpability of the materials at high temperature and pressure.

Another promising high temperature LCM was recently identified.[7] In this work, it was found that the addition of a cement, borax and glass fiber mixture to bentonite slurries produces a LCM that is pumpable at high tempertures as a result of the retardation resulting from the hydrolysis of the borax. A series of slot tests were completed in July. A series of larger-scale tests in the Sandia National Laboratory Lost Circulation Test Facility are scheduled for FY 1986.

3. Corrosion Resistant Elastomeric Liners for Well Casing

The geothermal fluids in the Imperial Valley are characterized by brines with high levels of corrosive substances. This drives the operators to using super alloys for routine components such as tubing and piping. This can be extremely expensive, suggesting the use of the process industry practice of lining pipe to protect it from corrosion, a perfect application for Y-267 EPDM.

DOE/BNL formed a cost sharing project with a geothermal operator to adapt the Y-267 EPDM for this application. Processing and adhesion to steel pipe are the primary technologies to be developed to be in a position to test the feasibility of the concept. Currently, no known system to bond the Y-267 EPDM to steel exists which can withstand the 288°C post-cure and the usually high temperatures associated with Y-267 EPDM applications. In addition, the uncured Y-267 EPDM is stiff and has no tack, making it difficult to lay up and mold onto the ID of pipe. The objective of this relatively small effort is to develop two (36 in.) lined prototype casing sections which can be field tested with actual brine flowing through them. The development of the prototypes is scheduled for completion in early 1986.

4. Geothermal Waste Utilization and Disposal

Before the large-scale development of geothermal energy can occur, environmentally and economically acceptable methods for the disposal of large quantities of waste must be developed. These wastes represent a large, low-grade domestic mineral resource. If economic methods for recovery are developed, the wastes could provide an important source of strategically important metals as well as revenues comparable to those from electric power generation.

The initial phase of the DOE/BNL program consists of an assessment in which data pertaining to the following questions are being compiled.

- What are the applicable environmental regulations at the state level for the states of interest?
- What are the applicable federal environmental regulations pertaining to geothermal resources and to what extent will they be involved?
- Are any of the exisiting regulations expected to change? If so, what are the timeframes for resolving these issues?
- Evaluate the regulations for definitions of waste classifications and for standard/proposed tests required. How are some of these required tests formulated and why?
- What are the near/far term requirements for the disposal of these waste?
- What is the current state-of-the-art disposal practices for these wastes?
- Can the operators of the geothermal projects meet the current regulation requirements and waste disposal standards? Are current disposal practices adequate? Will these companies need more time to develop additional or alternative disposal methods?
- What are the types of wastes generated from geothermal processes?

Two experimental approaches which are complementary are being used in attempts to develop methods which will economically meet the disposal regulations identified above.

The first is the use of biochemical techniques to concentrate and remove toxic metals from wastes, and the second is to develop processes for converting toxic constituents from the wastes into nonleachableforms which can be used as a construction material or disposed of in conventional landfill sites.

The initial results from the BNL studies on the biochemical treatment of wastes have recently been published.[8] These studies have demonstrated that certain microorganisms can grow in the presence of high concentrations of toxic metals in geothermal sludge and are able to bioaccumulate heavy metals. The bioaccumulation is selective and several microorganisms have been tested for selective adsorption of uranium, thorium, cobalt, chromium, manganese, tin, and platinum. The results have shown that under the experimental conditions used, *P. aeruginosa* SCU has a preference for uranium, while *P. aeruginosa* PAO-1 and *P. fluorescens* exhibit a preference for thorium, and *Aspergillus niger* is selective for chromium and thorium.[8] Currently the *P. aeruginosa* is being used as a model system to study mechanisms by which the toxic metal resistances are manifested at the molecular level. Concurrent studies address the bioaccumulation mechanisms. While the metal resistance is specific and plasmid mediated, the surface selectivity may be related to resistance, or may be due only to the chemical structure of the cell wall and cell membrane components. The results support the view that in the metal-microorganism interactions, several mechanisms may be operative, which involve specialized metabolites, such as exo-cellular chelators, specific cell surface sites, and transport agents.

With regard to the conversion of toxic wastes into nonleachable forms, several inorganic and organic encapsulants have been tested. Materials used include methylmethacrylate, polyester, sulfur, magnesium polyphosphate cement, and portland cement. Other variables included water content, particle size, and method of encapsulation. Preliminary results indicated that several systems had leach rates well below those specified in the State of California regulations. Work to optimize the processes and to estimate costs is in progress.

5. Materials for Nonmetallic Heat Exchangers

This project is investigating thermally conductive polymer-based composites for use as corrosion resistant materials of construction for shell and tube heat exchangers in binary geothermal processes. Corrosion of the brine side of tubing in shell and tube heat exchangers has been a major problem in the operation of binary geothermal processes. Compared to the cost of high alloy steels, a considerable economic benefit could result from the utilization of a proven corrosion resistant polymer concrete material if sufficient heat transfer properties can be derived. The work consists of determinations of the effects of compositional and processing variables on the thermal properties of the composite, and measurements of the physical and mechanical properties after exposure to hot brine and isobutane.

To date, the maximum thermal conductivity obtained is 3.5 BTU/hr-ft-°F, compared to a value of 11.2 BTU/hr-ft-°F for the AL 29-4C ferritic stainless steel used in the tubes of the Heber heat exchangers. Assuming all other design factors equal, direct substitution of the polymer composites for the metal tubes will reduce the rating of the exchangers by ~12%. However, anticipated reductions in the fouling resistance of the polymer composite tubing may compensate for the thermal conductivity differences.

For the Heber binary plant, it has been reported that the heat exchangers and condensers represent ~30% of the total investment in plant equipment.[9] Therefore, since the cost of the polymer composite tubing is estimated to be in the same range as that for carbon steel, substitution for the AL 29-4C could significantly reduce the cost of future binary plants.

6. Corrosion in Binary Geothermal Systems

This program yields corrosion data from laboratory and plant tests for metals presently used in binary plants and other more potentially resistive metals and nonmetals. In operating binary processes, brine leakage into the organic working fluid side of the plants has resulted in unanticipated corrosion problems. Data are not available on the effects of salt, oxygen, and water impurities in isobutane and/or isopentane on the corrosion rates of metals. The work involves the exposure of test coupons in operating plants and in a laboratory test loop in which the levels of water, oxygen and salt can be varied. When completed, the program will yield quantitative information regarding the extent of corrosion that will occur upon contamination of the binary side of a plant, thereby allowing designers materials options.

CONCLUSIONS

The DOE Geothermal Materials Program is addressing problems whose solutions have a short to moderate term impact on the operation of prototype plants as well as conducting long-term R and 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 are being used or tested by industry. Current R an D efforts on dynamic seals, lost circulation control materials, and lightweight well cements may be used by industry in the near future. Other efforts on elastomer-lined well casing, encapsulation or biochemical concentration and separation of wastes, and nonmetallic heat exchanger tubing will require considerably longer development times.

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