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Materials for Geothermal Production

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ABSTRACT

Advances in the development of new materials continue to be made in the Geothermal Materials Project. Many successes have already been accrued and the results used commercially.

In FY 1991, work was focused on reducing well drilling, fluid transport and energy conversion costs. Specific activities performed included lightweight CO₂-resistant well cements, thermally conductive and scale resistant protective liner systems, chemical systems for lost circulation control, corrosion mitigation in process components at The Geysers, and elastomer-metal bonding systems. Efforts to transfer the technologies developed in these efforts to other energy-related sectors of the economy continued and considerable success was achieved.

Laboratory testing of BNL-developed phosphate modified calcium aluminate cements confirmed their hydrolytic stability in 300°C brine and their resistance to chemical attack by CO₂. Specimens were found to be >20 times more resistant to carbonation than Class H cement and twice as resistant as unmodified calcium aluminate cements.

Testing of thermally conductive polymer cements as potential corrosion resistant liner materials for use in heat exchanger applications was continued. Field tests were conducted in flowing hypersaline brine and the results indicated scale deposition rates lower than those on a high alloy steel. Additional tests for bottoming cycle heat exchange use are planned for FY 1992.

Progress was also made with chemical systems for lost circulation control. If materials placement is to be performed by pumping through an open drillpipe or through a drillable straddle packer, a bentonite-ammonium polyphosphate-borax-magnesium oxide formulation, containing fibers or particulates when large fissures are encountered, can be used. This system was ready for demonstration in FY 1991, but a suitable test site did not become available. Optimization of this and three other formulations for use with other Sandia National Laboratories developed placement technology is being continued.

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Work to develop high temperature hydrolytically stable chemical coupling systems needed to bond elastomers to metal reinforcement commenced. Until these become available, it will not be possible to produce many important tools needed to reduce well-drilling costs. To date very promising results have been achieved using high melting point ($>280^{\circ}$) polyaromatic-type adhesives. Compared to the best commercially available coupling systems which will undergo complete disbondment from stainless steel upon exposure for 1 day to brine at 200°C , copolymers made from the polyaromatic materials show no disbondment or loss of bond strength after 5 weeks. Additional work is required to improve the magnitude of the bond and to improve the thixotropic behavior of the adhesives in the liquid state.

Cost-shared efforts with operators at the Geysers to evaluate the use of polymer concrete and polymeric liners to mitigate corrosion were continued. Small lined casing sections and full size collection piping tees are being tested. The results to date have been promising and larger-scale tests are planned.

INTRODUCTION

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, 2) reduce the costs of deep wells and directionally drilled wells by 10 percent, and (3) reduce well-cementing problems for typical hydrothermal wells by 20 percent.

If the GD program objectives are to be met, it is essential that new materials of construction be available. 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, drillpipe protectors, rotating head seals, and heat exchangers. In particular, improvements in lost circulation control, lightweight well completion materials, hydrolytically stable chemical systems for bonding high temperature elastomers to steel substrates, and downhole drill motors, would significantly reduce well costs.

As a result of the small and uncertain geothermal market, industry generally will not develop the special materials required for these critical components. Therefore, the purpose of the Brookhaven National Laboratory (BNL) project is to provide the technical and managerial basis for the performance of high risk/high payoff materials R&D so that the results are available to industry

in the near term. To date, the work has resulted in many materials advances which are now routinely^{1,2} used by the geothermal industry. These include high temperature elastomers,⁴ polymer cement corrosion protective liners,³ and well cements.

In FY 1991, R&D activities were focused on reducing well drilling, fluid transport, and energy conversion costs. Specific activities performed included lightweight CO₂-resistant well cements, chemical systems for lost circulation control, thermally conductive and scale resistant protective liner systems, corrosion mitigation in process components at The Geysers, and elastomer-metal bonding systems needed for use in high temperature well drilling and safety related applications. The work on bonding systems commenced during the year while the others were ongoing activities.⁵ Technology transfer efforts also continued. Major findings during FY 1991 and the thrusts of the current efforts are summarized below.

1. Advanced High Temperature Lightweight Cements

- o Phosphate bonded calcium aluminate cements >20 times more resistant to CO₂ than presently used cements.
- o Private sector downhole test locations identified.
- o Industry-initiated request for the formation of a Cooperative Research and Development Agreement (CRADA) being implemented.

2. Thermally Conductive Polymer Cement Liners

- o Field test with Salton Sea brine under heat exchanger conditions completed.
- o Compared to AL-29-4C, PC-lined tubing had a reduced fouling coefficient.
- o Durability and corrosion protective effectiveness of liner verified.
- o Industrial interest for continued evaluation.

3. Chemical Systems for Lost Circulation Control

- o MgO-based formulations ready for larger-scale laboratory and/or field testing.
- o Commenced development of potentially superior CaO-Al₂O₃-based systems.

4. Corrosion Mitigation at The Geysers

- o Based upon FY 1990 field test results, laboratory optimization of polymer cement formulations completed.
- o Cost shared field test program continued with two steam producers.
- o Lined well-head and transport line components in test.

5. High Temperature Chemical Coupling Systems

- o Identified acryl-type polymers and mixtures of same as promising coupling systems.
- o Hydrothermal stability in 200°C brine established.
- o Elastomer/adhesive/metal failure mechanisms determined.

6. Technology Transfer Activities

- o Commercial utilization by gas utilities.
- o Gas Research Institute R&D on condensing heat exchangers.
- o Long Island Lighting Co. R&D on corrosion protection for air preheaters.

RESULTS

1. Advanced High Temperature Lightweight Cements

The service life of a geothermal well is highly dependent upon the quality of the well cementing operation, and as drilling environments become more hostile, constraints resulting from the lack of high performance lightweight cements become more acute. Therefore, 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 CO₂-resistant lightweight high temperature cements. These improvements will help to transfer well-life limitations from materials to reservoir constraints in a cost effective manner.

Ideally, a cement for geothermal well completions should have the following properties: 1) slurry density <10 lb/gal, 2) bulk density <62.4 lb/ft³, 3) compressive strength at 24 hr age >1000 psi, 4) permeability to water <0.1 m Darcy, and 5) bond strength to steel casing >10 psi. In addition, the slurry should be pumpable by API standards for >4 hr at 150°C, be compatible with drilling mud, after curing be resistant to carbonation and brine, and non-corrosive to steel casing. A cost of <\$10/bag is also desired.

During FY 1991, work to formulate and test lightweight CO₂-resistant cements continued. Plans to initiate a Cooperative Research and Development Agreement (CRADA) with a geothermal producer and a service company for work on lightweight cements were formulated, and review procedures by all parties are underway.

In FY 1990, phosphate modified calcium aluminate cements were identified as promising CO₂-resistant binders for lightweight cements. This work was continued in FY 1991 and the results published in the Journal of the American

Ceramic Society.⁶ The results from this study concluded that rapid-setting phosphate bonded cementitious materials which are not susceptible to hydrothermal-induced hydrolysis can be prepared by mixing at room temperature calcium aluminate cement and Poly-N fertilizer containing ammonium dihydrogen monobasic orthophosphate as the major phosphate component. After curing for 1 hr at room temperature, compressive strengths >3,000 psi are obtained. When cured in a hydrothermal environment at 200°C for 24 hr, compressive strengths >10,000 psi, 10 times greater than the American Petroleum Institute (API) criterion, are achieved. At 300°C, changes in the crystal size of the cement microstructure result in strength reductions to ~6,000 psi.

Laboratory testing to measure the rate of carbonation of the cements and cements containing set retarders was performed and the results submitted for publication.^{7,8} The data from autoclave tests conducted in sodium carbonate-saturated brine at 300°C indicated that phosphate modified calcium aluminate cements retarded with borax to make them pumpable as defined by API standards, are ~20 times more resistant to carbonation than class H cement and twice as resistant as unmodified calcium aluminate cements. The cements are pumpable for 4 hr at 150°C. It was also determined that the inclusion of conventional organic-type retarders results in pumpable slurries, but the retarders undergo carbonation reactions. Also, inorganic acid retarders are not as effective for extending pumpability as organic ones, but they do not react with CO₂.

Downhole testing of BNL-supplied cements being performed as a cost-shared cooperative effort with the Department of Scientific and Industrial Research (DSIR) in New Zealand was continued throughout the year but it has not been possible to retrieve any of the samples for evaluation due to a partial collapse of the well casing as a result of corrosion. This problem makes it extremely unlikely that any additional data will be accrued from this test series. Attempts to locate alternative downhole test capabilities in high CO₂ environments appear to be successful and these tests should start this year (FY 1992).

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 liner materials for heat exchanger tubing. This activity investigates the use of thermally conductive composites for that application. The following material goals have been established: 1) heat transfer coefficient and surface roughness similar to those of AL-29-4C tubing, 2) fouling factor <50% of AL-29-4C when used in brines typical of the Salton Sea KGRA, and 3) cost not more than 100% greater than that of carbon steel.

Corrosion of the brine side of tubing in shell and tube heat exchangers can be a major problem in binary plants unless very expensive high alloy steel 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.

After completion of assembly and "base line" testing at the Geothermal Test Facility (GTF) by Idaho National Engineering Laboratory (INEL) personnel, a prototype shell and tube heat exchanger containing 80 ft of thermally conductive polymer cement lined carbon steel tubing (PCL) was assembled and placed in test at the Del Ranch geothermal power plant operated by Red Hill Geothermal. The fluid used in the test was at a temperature of 178°C and had a salt content of >275,000 ppm. Under heat exchange operations, its scaling and silica deposition rate was estimated to be 5 in./yr.

Considerable difficulty was encountered when attempts were made to operate the PCL heat exchanger and a conventional high alloy steel (AL-6XN) tubed unit over an extended period of time. These difficulties were due to the service handling problems associated with the brine at this facility, in particular, its supersaturation with silica.

Preliminary examination of the data indicated that the high alloy steel tube fouled to the point where the overall thermal resistance approximately doubled during ~250 hr of operation. Most, if not all of this increase was attributed to fouling on the brine side of the tubing since little fouling on the cold water side of the AL-6XN tubes was detected.

The data from the test loop containing the PCL tubes also indicated a doubling of the thermal resistance during a similar operating time. However, appreciable amounts of scale were detected on the outside (cooling water side) of the PCL carbon steel tubes. Therefore, the degree of fouling on the PC surface was less than that on the high alloy controls, but the differences were not quantifiable. The PCL tubing was cut into sections and returned to BNL for examination. Visual inspection of the PC liner indicated it to be non-uniform in thickness and very rough. No corrosion of the carbon steel substrate under the liner was apparent, thereby confirming the impermeability of the PC. When these examinations are completed in FY 1992, a joint INEL/BNL final report will be prepared. This report will summarize the thermal and hydraulic performance results from testing at the GTF, and the results of the testing at the Del Ranch plant. The latter will include the results from the post test examinations, and a review of the thermal performance of the tubes.

Based upon the results obtained to date, Red Hill Geothermal will participate in a cost shared effort with INEL and BNL to evaluate the PCL for use in bottoming cycle heat exchange applications. It is expected that 1-in. diameter tubing, as opposed to the 0.75-in. diameter material used in the earlier work, will be used in these tests which will take place in mid FY 1992. Prior to the preparation of the four 20-ft. long test sections, laboratory work to improve the centrifugal casting process to yield a smoother and more uniform liner will be conducted.

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. Analyses indicate that significant cost reductions can be made if advanced high temperature chemical formulations which, depending upon the fissure size, can be used with or without particulate fillers to rapidly plug lost circulation zones. The greatest cost reduction can

be attained if it is not necessary to remove the drillbit during the repair operation. In this case, potential cost savings compared to the costs for conventional two-plug cement treatments range from 47 to 78%.

The objective of this project activity is to develop advanced cementitious materials that meet the following criteria: 1) viscosity of individual reaction streams <70 Bc for 6 mo at temperatures <50°C and for ≥24 hr at 50° to 300°C, 2) viscosity of mixed reactants <70 Bc for 4 hr at 300°, 3) compressive strength >500 psi at 2 hr age, 4) permeability to water <10⁻² Darcy, 5) volume increase upon curing, 6) durability in brine at 300°C >30 days, 7) all constituents environmentally benign, 8) compatible with organic and inorganic particulates, and 9) materials cost <\$10/bbl.

During FY 1991, 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. For placement at temperatures >60°C, microencapsulation of the magnesium oxide in organics was determined to be an effective method for controlling pumpability. The formulations are currently being optimized with respect to placement and formation temperatures and the resultant mechanical properties of the cured cements.

Exploratory experiments were started with three other cement systems: CaO·Al₂O₃-bentonite-ammonium phosphate-borax, CaO·Al₂O₃-CaO(Al₂O₃)₂-bentonite-ammonium phosphate-borax, and class H cement-bentonite. In FY 1992 the most promising formulations from these systems will be selected for optimization with respect to various placement methods and formation conditions. If successful, commercial suppliers and users of the advanced materials will then have a choice of one or more formulations which can be selected on the basis of existing field conditions and cost.

Six potential methods for placement of the advanced chemical systems into fractured zones have been identified by SNL. These are listed below: 1) pumped through open drillpipe, 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 packer, and 6) pumped through drillstring - deployed porous packer. For each method the pumpability requirements, material quantities, setting times, and operating temperatures were estimated and these needs are being matched with the laboratory identified materials characteristics. Advanced high temperature MgO-based rapid setting materials suitable for placement using methods 1, 2, and 6 appear to be ready for demonstration today. Materials for use with methods 3-5 require additional optimization in FY 1992, but should be ready for prototype testing late in FY 1992 or in FY 1993.

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.

Cooperative cost-shared work performed at the Geysers with the Coldwater Creek Operator Company and the Northern California Power Authority (NCPA) continued throughout the year. Materials goals are as follows: 1) corrosion rate in pH 3 HCl-containing steam condensate at 200°C of <10 mils/yr and 2) cost less than twice that of mild steel. Based upon the results from tests conducted by Coldwater Creek Operator Company in late FY 1990 which indicated that polymer cement (PC) composite systems can provide corrosion protection to geothermal well casing upon exposure to condensing acidified steam environments, a series of laboratory tests were performed to optimize the system with respect to the exposure conditions. In this work which was completed in FY 1991, several series of test samples were exposed in autoclaves to pH 2 HCl solutions at 90°C for 3 mo. and to pH 2 HCl acidified steam at 200°C for 6 mo. Two monomer formulations and two filler systems were evaluated. The monomer formulations were a styrene-trimethylolpropane trimethacrylate (TMPTMA) system and a vinyl ester resin-TMPTMA system. The two filler systems had the same general mix design, however, one system contained Type III portland cement and the other contained class H well cement. The general formulation of the PC mixes was as follows: 14 to 16 wt% monomer, 86 to 84 wt% blended fine aggregate. In general, the blended aggregate system consisted of graded silica sand and cement. The results from both the acid and steam exposures indicated that all four systems performed well, exhibiting little or no deterioration and minimal loss of strength.

Concurrent with the above work, the effectiveness of polyphenylene sulfide (PPS) polymer as an acid resistant coating when applied to mild steel surfaces containing a polyacrylic acid-modified zinc phosphate conversion coating as a bonding agent, was also evaluated. After 3 mo autoclave exposure to pH 2 HCl at 90°C, this system also displayed good durability.

Based upon these promising results, field tests were resumed at the Coldwater Creek Operator Company site at the Geysers. The effort involved the testing of several 1-in. diam by 7.5 in. long carbon steel nipples which were lined at BNL. Two PC liners were tested; one was a styrene-TMPTMA system made with Type III portland cement and the other was a styrene-TMPTMA system made with class H well cement. The PPS coating was also tested. The nipples were tested by inserting them into the well head fluid stream perpendicular to the flow. The temperature of the stream was approximately 177°C and the velocity was about 200 ft/sec. The nipples were subjected to occasional abrasive attack resulting from particular matter within the stream. The nipples were returned to BNL for detailed evaluation in FY 1992. Preliminary visual inspections indicated little if any erosion or chemical attack on the PC samples. The PPS-lined nipples contained regions where the polymer had been removed, probably due to abrasion by particulates in the steam.

Additional field tests are planned for FY 1992. The first series will consist of four lined 8-in. diam. by 12-in. long wellhead sections. Two will be lined with a PC selected on the basis of FY 1991 results, the others with PPS. These tests are scheduled to commence in the second quarter of FY 1992.

The field tests initiated at the NCPA facility involve the testing of two 12-in. diam "T" sections which were lined with PC at BNL and then sent to the facility for testing. Both "T" sections were lined with a 3/16-in. thick PC made with the styrene-TMPTMA system containing the Type III portland cement. One of the liners also contained 1/4-in. long graphite fibers. The fibers were added to the system in an attempt to control shrinkage cracking of the liner mix.

5. High Temperature Chemical Coupling Systems

BNL provides liaison services to Sandia National Laboratories (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 member companies. In the course of this work, it was determined that the unavailability of a hydrolytically stable chemical coupling system needed to bond high temperature elastomers to metal reinforcement prevented the successful development of a drillpipe protector which would meet GDO specifications. The development of advanced blow-out-preventors and Moineau stators for downhole pump applications is expected to be impacted similarly.

As a result of this materials constraint, BNL initiated work in FY 1991 to develop advanced coupling systems that meet the following criteria: 1) peel strength >40 psi on mild steel and stainless steel, and 2) hydrothermal stability after 90 days in brine at 300°C. Specific end-use requirements for the coupling systems are summarized below:

Drillpipe Protectors

No loss of bond after 48 hr in brine at 290° and 5000 psi or in steam at 260°C and 660 psi while rotating at 100 rpm under a radial load of 3500 lb.

Rotating Head Seals

No loss of bond after 24 hr in brine at 240°C and 425 psi, or in steam at 200°C and 130 psi.

Blow-out Prevention Seals

No loss of bond after 90 day exposure to brine at 250°C and 450 psi, or in steam at 200°C and 400 psi.

The work has been separated into three elements: 1) elemental alteration and transformation of zinc-phosphate crystal coatings for use as high temperature protective coatings on steel and to enhance bonding with the coupling system, 2) coupling adhesives which produce hydrothermally stable polymer-metal interfaces, and 3) characteristics of polymer-elastomer interfaces after exposure to hydrothermal environments. Work in each element is performed concurrently.

Two polyaromatic-type adhesives, polyphenyletheretherketone (PEEK) and polyphenylethersulfone (PES) and copolymers made from mixtures of the polymers were selected for initial studies. The melting points of these polymers are 345° and 285°C, respectively, and they form high strength acid resistant adhesives.

Specimens which consisted of Y267 EPDM elastomer bonded to stainless steel using PEEK exhibited peel strengths ranging between 5 and 14 lb/in². These values were promising, but 3 to 8 times lower than that needed for drillpipe protectors. Failure normally occurred at the elastomer-adhesive interface. Curing of the elastomer under the conditions generally used by the elastomer industry may improve this bonding. More importantly, compared to the best commercially available bonding system which upon exposure to brine at 200°C for 1 day will undergo complete disbondment from stainless steel, bonding systems

composed of copolymers made from PEEK-PES mixtures undergo no disbondment or loss of bond strength after 5 weeks. For drillpipe protectors, stability for a minimum of 48-hr is desired.

BNL is currently attempting to increase the magnitude of the bond between the coupling adhesives and the metal substrate by chemically modifying the metal surface. Increases in both physical and chemical bonding are desired. Recent tests have given extremely promising results. It has been found that the application of a 1 to 2 micron thick polyelectrolyte-modified zinc phosphate conversion coating to the steel prior to the application of the coupling system increases the bond strength by ~30%. In addition, upon exposure to high temperature low pH acid environments or electrochemical attack, both of which will result in rapid deterioration, the surface modified-metal-coupling system interface remains stable. The measured delamination rate was ~150 times lower than that of the coupling agent-steel control. This work is continuing. All results to date have been compiled in a report⁹ which is currently under internal review prior to submission to a peer-reviewed Journal.

6. Technology Transfer

In addition to the above activities which impact specific geothermal industry needs, efforts to transfer the technologies to other private sector organizations were continued. A noticeable success in FY 1991 was the transfer of work on polymer concretes for use as high temperature corrosion resistant construction materials. In this case the Consolidated Edison Company of New York is currently evaluating polymer concrete formulations similar to those being tested at The Geysers, as a means of solving corrosion problems in their steam district heating systems in New York City. Conventional steel reinforced portland cement concrete utility vaults are now used to house valves and other process equipment. This is unsatisfactory since steam leaks combined with the high ambient temperatures (100° to 200°C) within the vaults result in rapid deterioration of the concrete. Due to the high strength, impermeability and resistance to chemical attack, use of polymer concrete will result in reductions in the required thickness of the vault walls, thereby lowering costs due to weight reductions, prevent ground water leakage into the vaults, and eliminate corrosion of the reinforcing steel and concrete deterioration.

Previously (FY 1990), Consolidated Edison and the Brooklyn Union Gas Company acquired similar but lower temperature technology from BNL for use in gas distribution system utility vaults. Both utilities now routinely use polymer concrete vaults in their operations and commercial sources of supply have been identified.

Other active technology transfer linkages established in FY 1991 are with the Gas Research Institute on corrosion protective coatings for condensing heat exchangers, and the Long Island Lighting Company on corrosion protection for air preheaters in oil-fired electric generation plants. Field testing of prototype components for both applications will take place in FY 1992.

CONCLUSIONS

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 used commercially.⁹ In FY 1991, utility company sponsored "full cost" recovery programs based upon materials technology developed in this project were initiated on topics such as condensing heat exchangers, high temperature composites for utility vaults used in district heating systems, and corrosion resistant coatings for use in oil-fired electric generating processes.

In FY 1991 the DOE/GD-sponsored R&D project was focused on reducing well drilling, fluid transport and energy conversion costs. Specific activities being performed included lightweight CO₂-resistant well cements, chemical systems for lost circulation control, thermally conductive and scale resistant protective liner systems, corrosion mitigation in process components at The Geysers, and elastomer-metal bonding systems needed for use in high temperature well drilling and safety related applications.

Laboratory testing of BNL-developed phosphate modified calcium aluminate cements confirmed the hydrolytic stability of the materials in 300°C brine and their resistance to chemical attack by CO₂. Specimens retarded by the addition of borax to make them pumpable by American Petroleum Institute (API) Standards were found to be ~20 times more resistant to carbonation than class H cement and twice as resistant as unmodified calcium aluminate cements. They also meet most of the other API design criteria. It should be noted that care must be taken in the selection of a retarding system which is necessary to make the cements pumpable. Conventional organic-type retarders are very effective, but they undergo reactions with CO₂. Inorganic acids are not as effective for extending pumpability but they resist carbonation. More work remains on the selection of an optimum retarder. Plans to establish a "Cooperative Research and Development Agreement" (CRADA) which will result in further laboratory characterization and downhole testing in several geothermal environments are being formulated.

Initial field testing of thermally conductive corrosion resistant polymer cement liners in flowing hypersaline brine under heat exchange conditions has produced promising results. Compared to a high alloy steel (AL-6XN) control, lined carbon steel tubing exhibited less scale formation at the brine-liner interface after 250 hr of operation. No corrosion of the steel or deterioration of the liner was apparent, but additional work to improve the surface texture and uniformity of the liner when centrifugally applied to long lengths of small diameter tubing is required. Additional testing is planned for the current year.

Progress has also been made in the development of advanced chemical systems for lost circulation control. If materials placement is to be performed by pumping through an open drillpipe or through a drillable straddle packer, a bentonite-ammonium polyphosphate-borax-magnesium oxide formulation, containing fibers or particulates when large fissures are encountered, can be used. This system was ready for demonstration in FY 1991, but a suitable test site did not become available. Optimization of this and three other formulations for use with other SNL developed placement technology will be continued in FY 1992.

Work to develop high temperature hydrolytically stable chemical coupling systems needed to bond elastomers to metal reinforcement commenced in mid-FY 1991. Until these become available, it will not be possible to produce many important tools needed to reduce well drilling costs. To date very promising results have been achieved using high melting point ($>280^{\circ}\text{C}$) polyaromatic-type adhesives. Compared to the best commercially available coupling systems which will undergo complete disbondment from stainless steel upon exposure for 1 day in brine at 200°C , copolymers made from the polyaromatic materials show no disbondment or loss of bond strength after 5 weeks. Additional work is required to improve the magnitude of the bond strength and to improve the thixotropic behavior of the adhesives in the liquid state.

Cost-shared efforts with operators at the Geysers to evaluate the use of polymer concrete and polymeric liners to mitigate corrosion were continued. Small lined casing sections are being tested by the Coldwater Creek Operator Company and full-size collection piping tees by the Northern California Power Authority (NCPA). The results to date have been promising, and larger-scale tests are planned for FY 1992. If successful, the economic viability of wells currently undergoing severe corrosion problems may be restored, thereby helping to maintain electric generating capacity at The Geysers.

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