ENERGY CONVERSION TECHNOLOGY

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DISCLAIMER

HYDROTHERMAL ENERGY CONVERSION TECHNOLOGY

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The goal of the Hydrothermal Program is to develop concepts which allow better utilization of geothermal energy to reduce the life-cycle cost of producing electricity from liquid-dominated, hydrothermal resources.

Research in the program is currently ongoing in three areas:

- Heat Cycle Research, which is looking at methods to increase binary plant efficiencies.
- Materials Development, which is developing materials for use in geothermal associated environments, and
- Advanced Brine Chemistry, with work taking place in both the brine chemistry modeling area and waste disposal area.

The presentations during this session reviewed the accomplishments and activities taking place in the hydrothermal energy conversion program.

Lawrence Kukacka, Brookhaven National Laboratory, discussed advancements being made to develop materials for use in geothermal applications. This research has identified a large number of potential materials for use in applications from pipe liners that inhibit scale buildup and reduce corrosion to elastomers for downhole use.

Carl J. Bliem, Idaho National Engineering Laboratory, discussed preparations currently underway to conduct field investigations of the condensation behavior of supersaturated turbine expansions. The research will evaluate whether the projected 8% to 10% improvement in brine utilization can be realized by allowing these expansions.

Eugene T. Premuzic, Brookhaven National Laboratory, discussed advancements being made using biotechnology for treatment of geothermal residual waste; the various process options were discussed in terms of biotreatment variables. A treatment scenario and potential disposal costs were presented.

John H. Weare, University of California, San Diego, discussed the present capabilities of the brine chemistry model he has developed for geothermal applications and the information it can provide a user. This model is available to industry.

The accomplishments from the research projects presented in this session have been many. It is hoped that these accomplishments can be integrated into industrial geothermal power plant sites to assist in realizing the goal of reducing the cost of energy produced from the geothermal resource.

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 CO_2-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 CO_2. 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 test 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.

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°) 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, blowout 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 used by the geothermal industry. These include high temperature elastomers,[1,2] polymer cement corrosion protective liners,[3] and well cements.[4]

In FY 1991, R&D activities were focused on reducing well drilling, fluid transport, and energy conversion costs. Specific activities performed included lightweight CO_2-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 CO_2 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 $CaO\text{-}Al_2O_3$-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 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.

Ideally, a cement for geothermal well completions should have the following properties: 1) slurry density <10 lb/gal, 2) bulk density <62.4 lb/ft^3, 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 CO_2-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 CO_2-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 CO_2.

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 CO_2 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: $CaO \cdot Al_2O_3$-bentonite-ammonium phosphate-borax, $CaO \cdot Al_2O_3$-$CaO(Al_2O_3)_2$-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 con cerns 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 a 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 send 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/in^2. 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 report[9] 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 CO_2-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 CO_2. 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 CO_2. 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°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.

REFERENCES

1. Hirasuna, A. R., et al., 1983, A proven elastomer compound for extremely hostile geothermal and oilfield environments, IADC/SPE Drilling Conference, Paper 11407, New Orleans.
2. Gidanian, K. C., Hirasuna, A. R., and Stephens, C. A., 1988, Development of high temperature elastomer materials (DOHTEM) for use in dynamic sealing applications in geothermal processes, BNL 41873.
3. Kaeding, A. O., 1981, Design and fabrication of polymer concrete-lined pipe for testing in geothermal energy processes, Final Report, BNL 33019.
4. API work group reports field tests of geothermal cements, 1985, Oil and Gas Journal 94, 93-97.
5. Kukacka, L. E., Proc. DOE Geothermal Program Review IX, San Francisco, March 1991, DOE CONF-913105, Washington, 71-75, 1991.
6. Sugama, T. and Carciello, N. R. Strength development in phosphate bonded calcium aluminate cements. BNL 46263, J. Am. Ceramics Soc., 75, 5, 1023-30 (1991).
7. Sugama, T. and Carciello, N. R. Carbonation of hydrothermally treated phosphate-bonded calcium aluminate cements. Cem. and Conc. Res., in press.
8. Sugama, T., Gray, G., and Carciello, N. R. Influence of set-retarding admixtures on alkali carbonation of calcium aluminate cements under hydrothermal conditions. J. Mat. Sci. and Tech., in press.
9. Miura, M. Carciello, N. R., and Sugama, T. Determination of physico-chemical parameters affecting elastomer-stainless steel joints using polyaryl adhesives. Manuscript in preparation.
10. Proc. DOE Geothermal Program Review VIII, San Francisco, April 1990, DOE CONF-9004131, Washington, p. 191, 1990.

SUPERSATURATED TURBINE EXPANSIONS FOR BINARY GEOTHERMAL POWER PLANTS

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Abstract

The Heat Cycle Research project is developing the technology base that will permit a much greater utilization of the moderate-temperature, liquid-dominated geothermal resources, particularly for the generation of electrical power. The emphasis in the project has been the improvement of the performance of binary power cycles. The investigations have been examining concepts projected to improve the brine utilization by 20% relative to a "Heber-type" binary plant; these investigations are nearing completion. Preparations are currently underway in the project to conduct field investigations of the condensation behavior of supersaturated turbine expansions. These investigations will evaluate whether the projected additional 8% to 10% improvement in brine utilization can be realized by allowing these expansions. Future program efforts will focus on the problems associated with heat rejection and on the transfer of the technology being developed to industry.

Conventional binary cycles have used turbine expansions which occur totally within the dry vapor region. The Heat Cycle Research project is currently investigating the feasibility of turbine expansions which pass through the two-phase region in a metastable condition. Early work indicated that cycle performance could be increased over systems with dry turbine expansions for certain working fluids. These gains result because of better matching of the geofluid cooling curve with the working fluid heating curve in geofluid heaters in supercritical cycles, as well as a better match of the heat transfer between fluids in the condenser. Early studies indicated that no condensation would occur at the metastable conditions necessary for the performance increase. An 8% increase in the work produced per unit mass of geofluid is expected when these expansions are allowed. This will give a 2.2% reduction in capital equipment cost and a 5.5% reduction in the cost of producing electricity. Market penetration studies indicate a potential of 29% increase in geothermal power production in the next 20 years for resources in the 350 to 400 °F range.

Experimental work is currently underway at the Heat Cycle Research Facility to verify this concept. Working fluid will be expanded in a nozzle which simulates the flow in a turbine. A laser system will be used to detect droplet formation in the nozzle. Limiting turbine inlet states for which droplets will not form in the turbine will be determined. A reaction turbine will subsequently be operated within this performance envelope to confirm the feasibility of this concept with actual hardware.

Background

The objective of the Heat Cycle Research Project is to develop, or promote the development of, technology which will result in a more effective utilization of moderate temperature geothermal resources. The emphasis of the program to date has been directed towards the binary cycle technology which more effectively utilizes the energy contained in the liquid-dominated, moderate-temperature hydrothermal resources. The project is also defining the technology need to utilize resources having technical or institutional barriers to development.

During the scoping and analytical studies in the initial phases of the program, several concepts were identified which showed significant potential for performance improvements. These concepts were, and continue to be, the subject of field investigations conducted by the project with a small binary plant. These field investigations, which were initiated over 10 years ago at the Raft River site in southern Idaho, have been carried out at geothermal facilities in the Imperial Valley of southern California since the mid-1980's. The small plant used for these investigations, referred to as the Heat Cycle Research Facility (HCRF), is shown schematically in Figure 1. The plant contains most, if not all, of the components found in a typical binary power plant. The components are designed to allow the specific concepts/ components under consideration, to be investigated. The design of the facility allow for components to be readily changed; its size allows these changes to be made at reasonable costs, while maintaining component configurations similar those that would be found in a commercial facility.

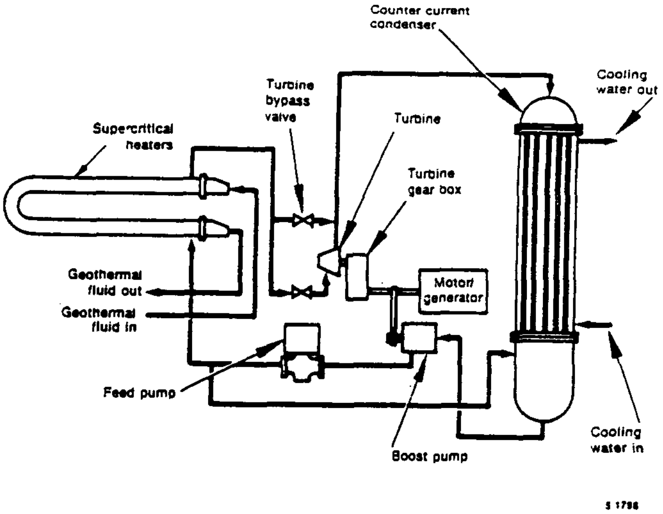

Figure 1. Schematic of the Heat Cycle Research Facility

As indicated, analytical studies[1-4] conducted projected significant performance gains could be achieved relative to a reference plant. For these studies, the conditions at the Heber binary plant were selected as the reference plant; it was felt this plant represented the "state-of-the-technology" at that time (this assumption appears to continue to be valid). Relative to the Heber-type plant, the studies indicated that performance improvements of 20% to 30% (in terms of the net power produced per unit brine flow rate, or brine effectiveness) were possible. Utilization of supercritical cycles with optimized selection of a working fluid mixture and turbine inlet conditions provided the significant portion (20% of the total 30%) of the performance improvement. The improvements result from taking advantage of the non-isothermal phase changes that occur when mixtures are used (this characteristic reduces the irreversibilities during the heat transfer processes). In order to take advantage of this working fluid characteristic, the heat exchangers must be designed for, and operate with, counter-current flow paths and integral phase changes. By vaporizing the mixture at supercritical pressures, the concerns relative to being able to achieve "integral" boiling would be alleviated; the HCRF heaters were designed accordingly. The HCRF condenser was design for in-tube condensing and a vertical tube orientation; this design was felt to provide the best opportunity to achieve the countercurrent "integral" condensation necessary to achieve the performance gains.

It was projected that the remaining performance improvement (approximately 10%) could be achieved by allowing supersaturated turbine expansions with the advanced cycle.[5] In this type of expansion, the vapor enters and leaves the turbine at conditions outside of the two-phase region. However, during the expansion process in the turbine, the fluid, if at equilibrium, would be two phase. Studies suggested that condensate droplets would not form, or if they did form would remain small (too small to damage the turbine internals or adversely effect performance). This is the current area of project activities.

This work is being done as part of the Heat Cycle Research program conducted by the Idaho National Engineering Laboratory. The work was supported the U. S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, Office of Utility Technologies under Contract No. DE-AC07-76ID01570. Mr. Raymond J. LaSala of the Geothermal Division is the program manager and Mr. David W. Robertson directs the program through the Idaho Operations Office.

Cycle Performance Improvement with Super-Saturated Expansions

Binary thermodynamic cycles used in the conversion of geothermal energy to electrical energy commonly utilize hydrocarbon working fluids (pure fluids or mixtures). The cycles generally have been structured to avoid turbine expansions into the two-phase region, fearing the effects of moisture in the turbine. (In these cycles, it is assumed that the working fluid will always be in thermodynamic equilibrium and that the formation of liquid during the expansion will occur according to thermodynamic equilibrium constraints.) This type of cycle, using supercritical heating, is shown in a temperature-entropy diagram in Figure 2 as 1-2-3-4-5-1. The working fluid depicted in the diagram is one which dries on expansion, such as isobutane or heavier alkanes or mixtures which have one of these as a major constituent. Note that as a result of avoiding the two-phase region superheating results.

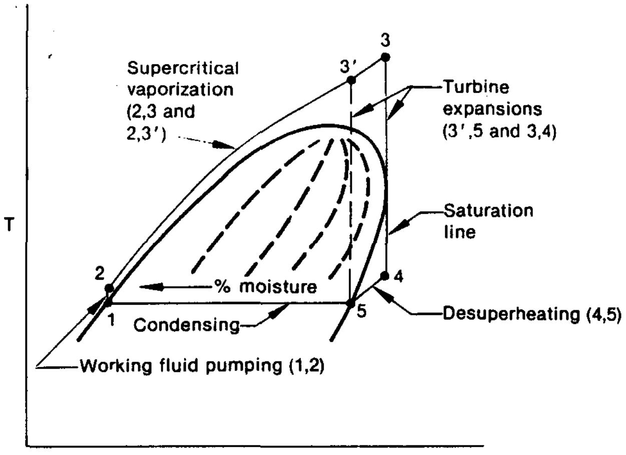

Figure 2. Binary Cycles Showing Two Types of Turbine Expansions

If the turbine inlet temperature could be decreased to 3', the cycle 1-2-3'-5-1 would occur. In this cycle, the turbine expansion goes through the two-phase (wet) region. Note for this cycle that there is no superheat in the turbine exhaust. This fact indicates that the irreversibility in the heat rejection process is probably smaller in the second cycle than in the first cycle, which avoids the two-phase region. Figure 3 shows the heating process on a temperature-enthalpy diagram for the two cycles. This figure shows the geofluid cooling curve for each cycle. In the cycle which expands through the two-phase region, the geofluid is cooled to a lower temperature than in the cycle which avoids the wet region. This indicates that the cycle which expands through the wet region should have a higher conversion efficiency than the cycle which avoids the region because there is less residual available energy in the geofluid which leaves the process. In addition, the temperature difference between the hot geofluid and the working fluid are smaller at the lower temperatures and greater at the higher temperatures. This indicates a smaller irreversibility in the heat addition precess. The irreversibility associated with the transfer of a given amount of heat at a given temperature difference at temperatures approaching the environmental temperature (low temperatures) is approximately twice that at the higher temperatures.[6] All of these attributes of the cycle with the turbine expansion through the two-phase region indicate that it will have a higher efficiency. In terms of the net geofluid effectiveness (net plant output, including heat rejection parasitic power per unit mass of geofluid), a system with a working fluid mixture of 96% isobutane and 4%

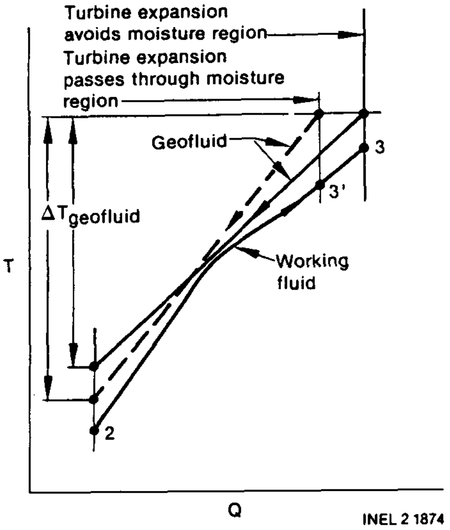

Figure 3. Heating Process for Binary Cycles With Two Types of Turbine Expansions

heptane (by mass) will improve its performance 8% if there is no change in turbine efficiency for the two turbine expansions.[1]

Prediction of Metastable Expansion

It is expected that the working fluid in a turbine expansion which passes through the wet region will pass through a series of metastable or supersaturated states and little or no condensation will result. Vapor condensation in steam turbines has been well characterized by the "Wilson Line" to estimate the extent to which supersaturated water vapor will occur in a near-isentropic turbine expansion. For water, the Wilson line is displaced in enthalpy about 55 Btu/lbm into the two-phase region from the saturated vapor line. It is generally shown on a Mollier diagram, an enthalpy-entropy plot. Above this line, the water vapor exists in a supersaturated vapor state. Condensation of the vapor during expansion occurs only below this line. In 1897, C. T. R. Wilson published an account of this behavior for water vapor.[7] This phenomenon was examined analytically by Keenan[8] who was able to predict the line for water.

Demuth, using methods similar to those of Keenan, studied organic working fluids such as isobutane.[5] He concluded that:

1. Condensation will not necessarily occur in the turbine expansions of interest.
2. Turbine expansions crossing the saturation line close to the critical point with a final equilibrium state which leaves the two-phase region, may initially show a tendency to condense very fine droplets (fog), but this fog will tend to evaporate as the expansion continues.
3. Turbine performance should not be degraded significantly as a result of these turbine expansions.

Some experiments were run at the Heat Cycle Research Facility using an impulse turbine with expansions which if isentropic would have passed through the two phase region. In these tests, no deterioration in the turbine efficiency was noted. These tests were short-term and some difficulty in precisely measuring the turbine output power was encountered. There was no trend away from a constant turbine efficiency as the expansions progressed further into the two-phase region.

The remainder of this report outlines plans for the experimental verification of the fact that turbine performance is not degraded by this type of turbine expansion and discusses the economic ramifications of this type of cycle.

Economic Impact of Supersaturated Turbine Expansions

Previous work[1,2] indicate that an 8% improvement in performance is expected for a cycle with a metastable turbine expansion through the wet region for a geothermal resource at 455 K (360 °F) using a mixture of 96% isobutane and 4% heptane for a working fluid. The capital cost of such a system may be greater than for a cycle which avoids the two-phase region. It is therefore not certain to what extent this performance increase will lower the cost of producing electrical energy. Demuth and Whitbeck[3] devised a method of estimating the changes in the cost of electricity resulting from changes in a plant configuration. This "Value Analysis" was used to explore the impact of the advanced concepts developed in the Heat Cycle Research Program on the cost of electricity.

Early studies Demuth[1,2] showed that permitting equilibrium states for the turbine expansion process to pass through the two phase region for a 96% isobutane/4% heptane mixture (with no geofluid outlet temperature constraint) resulted in a potential improvement in net geofluid effectiveness of approximately 8%. This study assumed fixed heat exchanger pinch points and used a shell and tube condenser and a wet cooling tower. Questions arise concerning the economic feasibility of this cycle because the mean temperature difference in the heater with a fixed pinch point will be lower for the cycle with expansion through the two phase region. In addition, no investigation has been made concerning a system which uses dry cooling (an air-cooled condenser).

A study[9] was undertaken to investigate the economic optimum for both dry and wet cooled systems. A system similar to the Mammoth Plant[10] was used in the study.

A number of results and conclusions of this study[9] are summarized below:

1. There is an economic benefit to systems using a metastable turbine expansion through the two phase region. For subcritical turbine inlet pressures, the reduction in the cost of electricity is not as great as for supercritical pressures, however it may still be worthwhile. For systems with shell-and-tube condensers and evaporative cooling towers, the reduction in the cost of electricity is greater than 8% over a similar system with a dry turbine expansion. For systems with air-

cooled condensers, the reduction is approximately 4.5%. IM-GEO[11], the computer model of the cost to produce electricity from U.S. geothermal hydrothermal liquid-dominated resources commissioned by the Geothermal Division of the U.S. Department of Energy, predicts decreases in cost of electricity around 4% for the Imperial Valley region.

2. For any system, there are potential gains possible in adjusting heater and condenser pinch points and condensing temperature. For a system with a subcritical turbine inlet state and a dry turbine expansion, the optimum system reduces the cost of electricity more than 8% over a system with 10°F pinch points.

3. Heater pinch points are generally increased in going from systems with dry turbine expansions to metastable expansions which go through the two-phase region because of the better fit between the geofluid and working fluid in the systems with metastable expansions. The optimum condenser pinch points and condensing temperatures are the same for both types of expansions.

4. Heater pinch points are similar for systems with both types of heat rejection systems while condenser pinch points are larger for the air-cooled case. The approach of condensing temperature to wet bulb temperature or dry bulb temperature depending on the type of heat rejection is similar for the two types of systems.

Experimental Verification of Supersaturated Turbine Expansions

Based on these studies, an investigative program is in underway to examine and study these types of expansions. The initial focus of this effort will be to investigate the condensation behavior of these expansions. These investigations will be carried out at the HCRF utilizing a laser detection system with two-dimensional expansion nozzle which simulates the turbine expansions of interest. This laser detection system (developed for the project by North Carolina A&T) will detect the scattering of a laser beam passed axially through the nozzle, by any condensation droplet present.[12] The experimental setup is shown in Figure 4.

In the laboratory it was possible to detect particles as small as 1 nanometer with this detection system (as a point of comparison, a single isobutane molecule has a size a little over 0.5 nanometers). The expansion nozzle has a glass window with photomultiplier tubes, which detect the light scattering, located along the length of the nozzle. The nozzle will be utilized in a loop by-passing the turbine at the HCRF. Nozzle inlet working fluid conditions will be varied to simulate the range of expansions of interest, ranging from completely "dry" expansions, to those where one would expect condensate to form. By identifying those turbine inlet conditions which promote condensation during expansion, it will be possible to determine how far into the two phase region these supersaturated expansions can proceed without the formation of droplets large enough to damage the turbine internals.

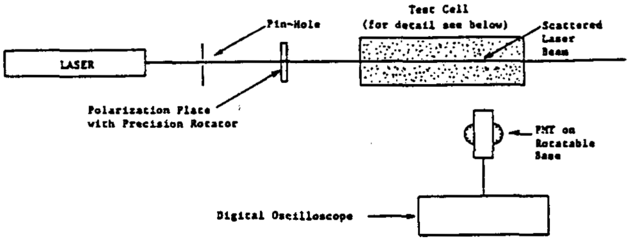

Figure 4. Schematic of Set Up for Measurement of Scattering Intensity of Particles.

In tests at the HCRF, the nozzle will replace the test cell as depicted in Figure 4. In conjunction with the testing of the nozzle, a single-stage, radial-inflow, reaction turbine will be installed at the HCRF. After utilizing the nozzle and laser detection system to "map" the turbine inlet conditions which result in condensate formation, this turbine will be used to investigate the impact of the super-saturated expansions on turbine performance. One manufacturer indicates that a reaction turbine can be operated "wet" without damage and high efficiencies. Both of these items will be elements of investigations at the HCRF with this turbine. The impact of the supersaturated expansions on the turbine efficiency will be examined, along with the impact, if any, of mixtures on performance. Prior to concluding these investigations, it is anticipated that the turbine will be operated with supersaturated expansions for an extended period. This test will specifically address whether there is any adverse affect with time on performance, or the turbine internals with these types of expansions.

Summary

The following summarize the present status of the Heat Cycle Research project:

* The investigations to date have shown that the proposed concepts that substantially increase the performance of binary cycles are thermodynamically possible. The assumptions required for the projected performance gains, have been validated with field investigations.

* The verification of assumptions made relative to the 8% to 10% performance improvements possible with supersaturated turbine expansions is in progress. These field investigations will determine whether the conditions promoting condensate formation are in present in the expansions of interest, and whether these expansions adversely affect the performance of the turbine.

* There is a practical limit to the performance of the binary power cycles, imposed by operating constraints of the cycle components. The performances of the supercritical cycles being studied in the project are approaching this practical

limit, as are the performance of other advanced binary power cycles.

The future project efforts will focus on the issue of improving heat rejection systems, particularly with regard to their consumptive use of water. Innovative schemes with the potential to reduce cooling water make-up or allow lower quality cooling waters to be used, will be examined and investigated.

As the development of the technology base to utilize the supercritical cycles under investigation nears completion, increased emphasis will be placed on industry's assimilation of this technology. This effort to transfer this technology to industrial users will be the major project emphasis prior to the anticipated project termination in the mid-1990's. The definition as to how this transfer will occur is a planned project activity for the next two years.

References

1. Demuth, O.J., "Analysis of Mixed Hydrocarbon Binary Thermodynamic Cycles for Moderate Temperature Geothermal Resources", EGG-GTH-5753, February 1981.

2. Demuth, O.J. and Kochan, R.J., "Analysis of Mixed Hydrocarbon Binary Thermodynamic Cycles for Moderate Temperature Geothermal Resources Using Regenerative Techniques", EGG-GTH-5710, November 1981.

3. Demuth, O.J. and Whitbeck, J.F., "Advanced Concept Value Analysis for Geothermal Power Plants", EGG-GTH-5821, March 1982.

4. Bliem, C.J., "Preliminary Performance Estimates of Binary Geothermal Cycles Using Mixed-Halocarbon Working Fluids", EGG-EP-7312, July 1986.

5. Demuth, O.J., "Preliminary Assessment of Condensation Behavior for Hydrocarbon Expansions Which Cross the Saturation Line Near the Critical Point", EGG-GTH-5960, July 1982.

6. Bliem, C.J. and Mines, G.L.,"Advanced Binary Geothermal Power Plants - Limits of Performance", EGG-EP-9207, December 1990.

7. C. T. R. Wilson, Phil. Trans., Vol. 189 (1897), pp. 265-307.

8. J. H. Keenan, Thermodynamics, New York: John Wiley & Sons, Inc., 1941, pp. 429-444.

9. Bliem, C. J. and G. L. Mines, "Economic Impact of Metastable Turbine Expansions in Binary Cycles Including Discussion of Future Related Work at the Heat Cycle Research Facility", EGG-EP-9827, (Presently being completed.)

10. R. G. Campbell and C. Harvey, "Expanding the Mammoth Geothermal Project", Geothermal Resources Council Bulletin, June 1991, pp. 162-165.

11. D. Entingh and L McLarty, "Geothermal Cost of Power Model IM-GEO Version 3.05: User's Manual", February 22, 1989.

12. Goswami, D.Y.,"A Laser Based Technique for Particle Sizing to Study Two Phase Expansion in Turbines", ASME International Solar Energy Conference, March 1991, Reno NV.

GEOTHERMAL WASTE TREATMENT BIOTECHNOLOGY: PROGRESS AND ADVANTAGES TO THE UTILITIES

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ABSTRACT

Development of biotechnology for treatment of geothermal residual waste is aimed at the application of low-cost biochemical processes for the surface treatment and disposal of residual geothermal sludges. These processes, in addition to the lowering of disposal cost, are designed to be environmentally acceptable. Recent studies at Brookhaven National Laboratory (BNL) have shown that optimization of several process variables results in fast rates (<24h) of metal removal from residual sludges at acidic pH (~1-2). Optimization of the process variables also enables the removal of radioactive isotopes. In addition, the aqueous phase produced during the bioprocessing which contains solubilized metals can be further treated in a manner which precipitates out the metals and renders the aqueous effluent toxic metal free. In this paper, the various process options will be discussed in terms of biotreatment variables. Chemical composition before and after biotreatment will also be discussed in terms of long-range effects, quality assurance and potential disposal costs.

INTRODUCTION

Systematic studies in this laboratory[1-5] have shown that a technically feasible and environmentally acceptable biotechnology for detoxification of geothermal residual sludges depends on several parameters, which include properties varying from reactor size and sludge loading to the chemical nature of salts and process temperature, all essential in the determination of cost-efficiency of the bioprocesses considered. Further, particular attention must be paid to the mode of sampling and type of analysis used as demonstrated by an analytical study of residual sludges from the Salton Sea area.[6] Studies of metal solubilization rates and thus the rates of their removal from sludges by multi-element techniques of analyses (i.e., 60 metals or more simultaneously) have shown consistently that in the initial phase 80% or more of metals are transferred from the solid to the liquid phase. Concurrent work in this laboratory has also shown that the metals can be recovered from the aqueous phase, rendering the liquid phase environmentally useful and acceptable. Current work at BNL is based on laboratory scale experiments which allows for process modifications essential to a cost efficient scaling-up strategy. Some of these experimental factors will be discussed in terms of multielement analyses and estimated waste disposal scenarios.

EXPERIMENTAL

Induced Coupled Plasma-Mass Spectrometry (VG-ICP-MS, Plasma Quad 2) was used routinely for all metal analyses. The instrument has a parts per trillion sensitivity and is capable of detecting and measuring simultaneously the concentration of up to seventy elements. The ICP-MS system detects different isotope masses and is particularly useful for mass numbers above 40. Typical results for lead, mercury, strontium, and rubidium are shown in Figures 1 and 2 for nontreated and biotreated samples. Because of the sensitivity and versatility of the analytical technique used several aspects of sampling and samples preparation discussed elsewhere have to be considered.[7] The bioreactors used in the studies reported in this paper were of the agitated tank and fluidized bed type already described in another paper.[3] It is to be understood that laboratory bioreactors serve as models for process scaling-up. Such bioreactors serve also as test systems for reactor design and offer versatility in the study of

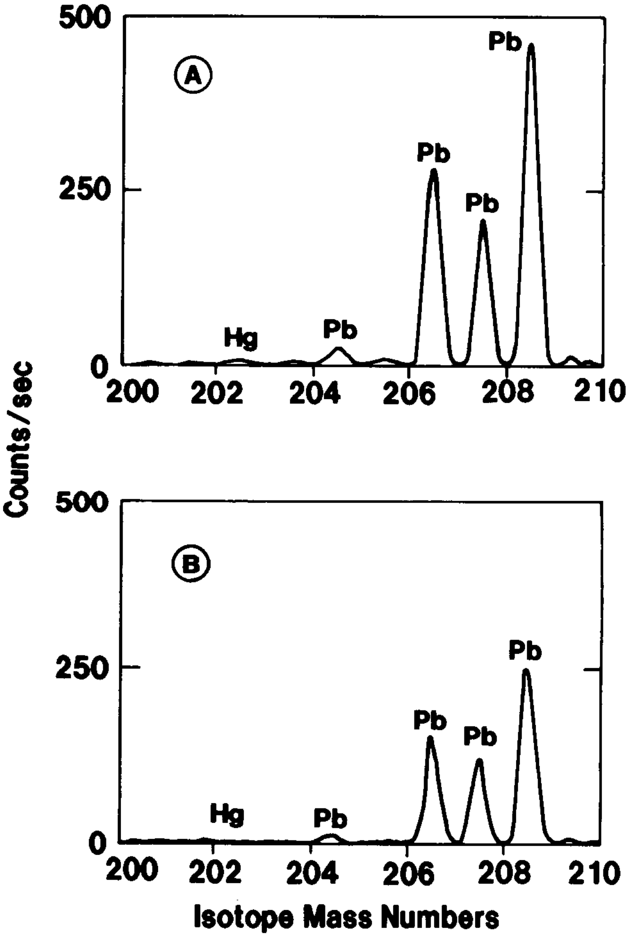

Figure 1. ICP-MS Analysis for Mercury and Lead. 'A' before and 'B' after Biotreatment.

processes as well as materials needed for bioreactor construction. This is particularly important in view of the corrosive conditions under which the detoxification process operates. Typically, the lab-scale (from 5 to 60 liters) bioreactors serve as models for a biochemical waste treatment plant shown in Figure 3. In this type of a plant, the fluidized bed and the agitated tank bioreactors are interchangeable.

RESULTS AND DISCUSSION

Multielement Kinetic Studies

Results of several simultaneous multielement kinetic studies are shown in Figures 4 and 5. All are consistent with previous reports (e.g., 3) and show that at 55°C there is a rapid removal of metals at a 40% sludge loading. All of the analyses are given for the fluidized bed and agitated tank bioreactor. Although programmatically we are not studying the mechanisms of solubilization, some mechanistic aspects have to be considered, particularly in the cases of less soluble metal salts. Therefore, the initial rates for uranium, lead, and thorium have been re-examined over a 10 hour period of time and the results are shown in Figures 6 and 7. These results clearly show that even for less soluble salts a solubilization of 30% to 60% can be achieved very rapidly. The possibility of using fast kinetics and short residence times (i.e., less than 10 hrs) is now being explored. Similarly, microorganisms which use other electron pools for their oxidation-reduction process are also being explored, because under optimum conditions such processes allow for high solubilization of less soluble salts.

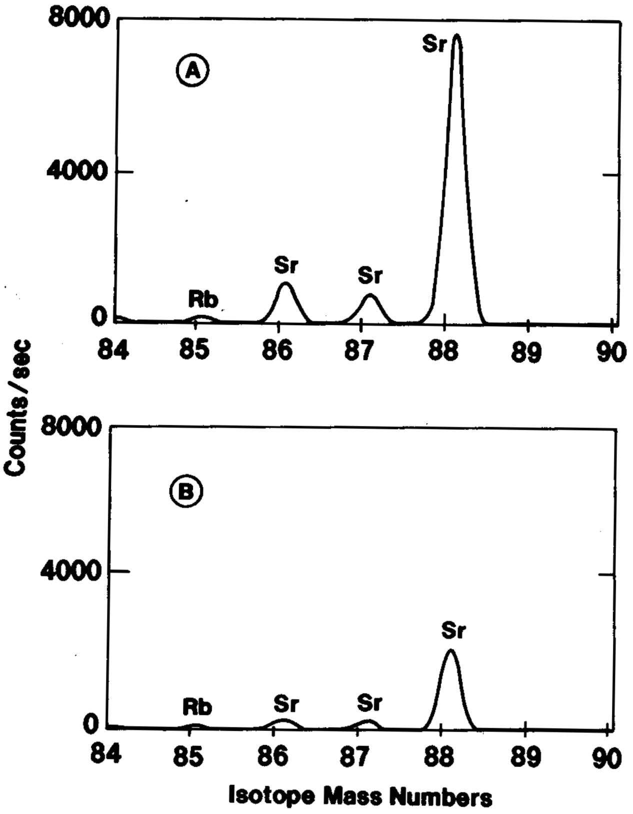

Figure 2. ICP-MS Analysis for Rubidium and Strontium 'A' before and 'B' after biotreatment.

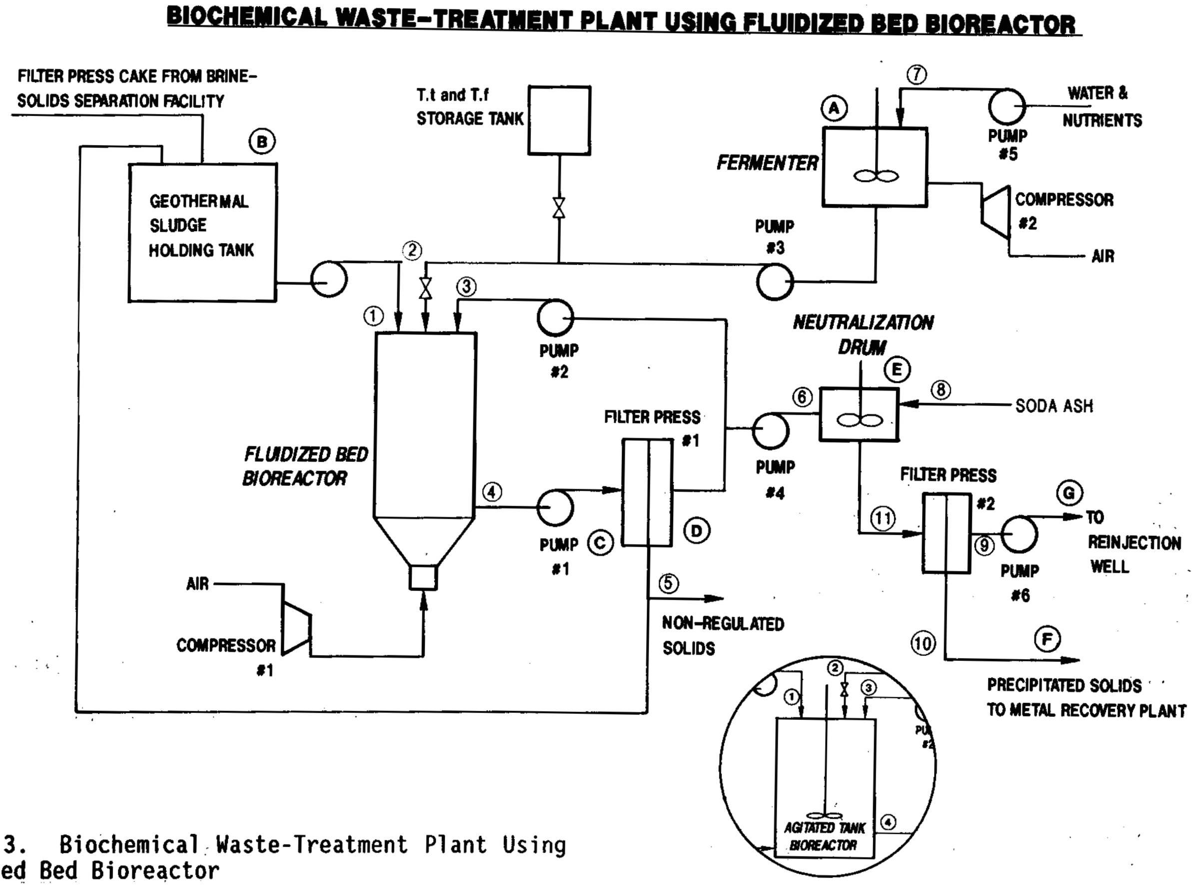

Figure 3. Biochemical Waste-Treatment Plant Using Fluidized Bed Bioreactor

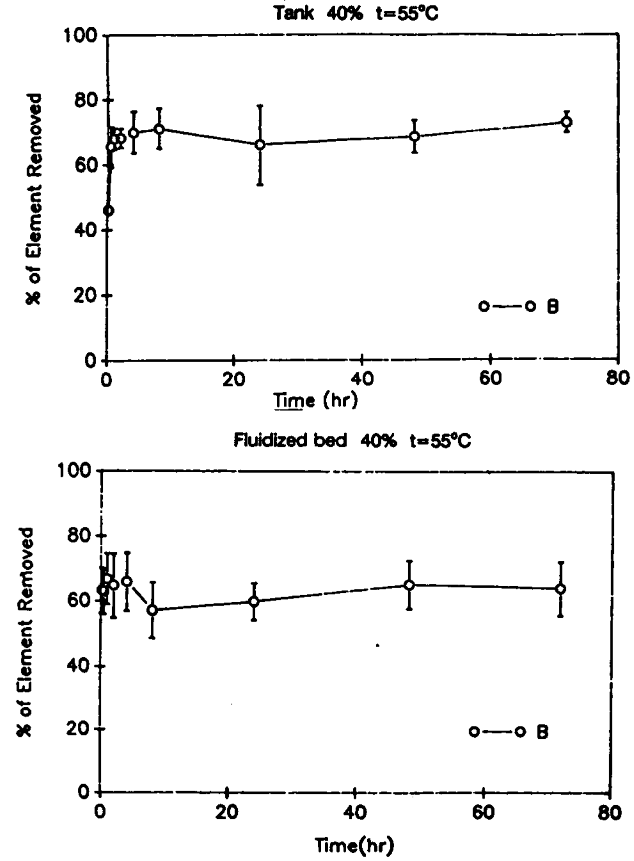

Figure 4. Removal of Boron.

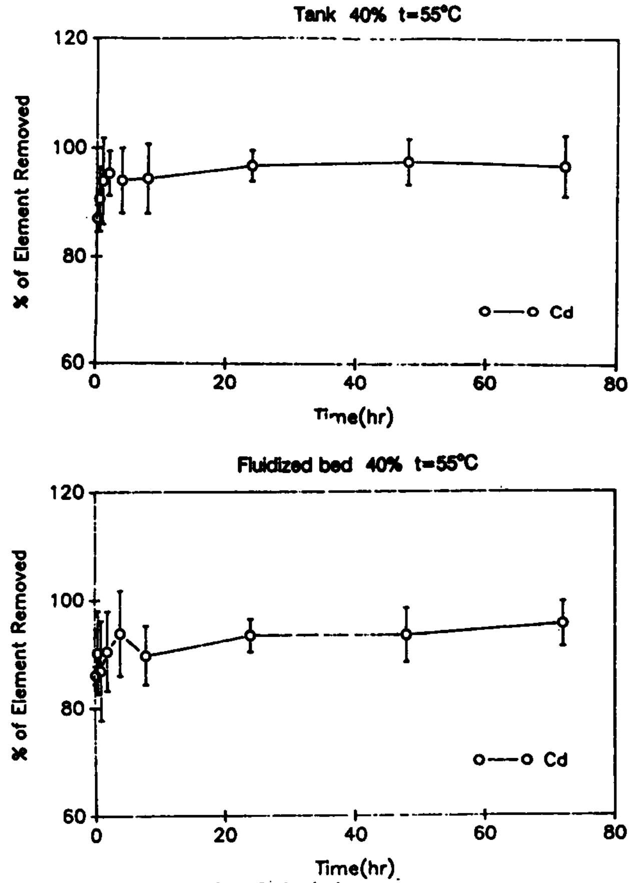

Figure 5. Removal of Cadmium.

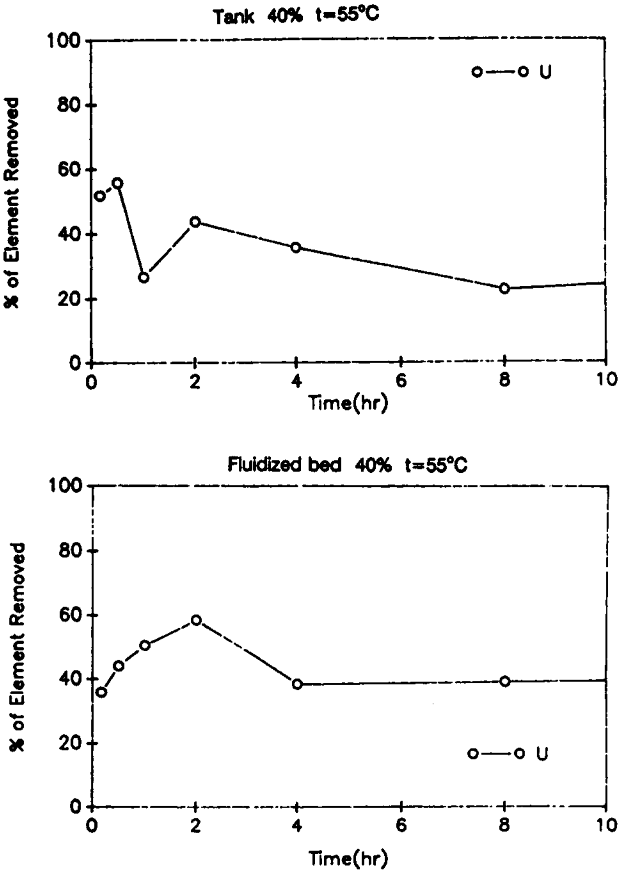

Figure 6. Removal of Uranium.

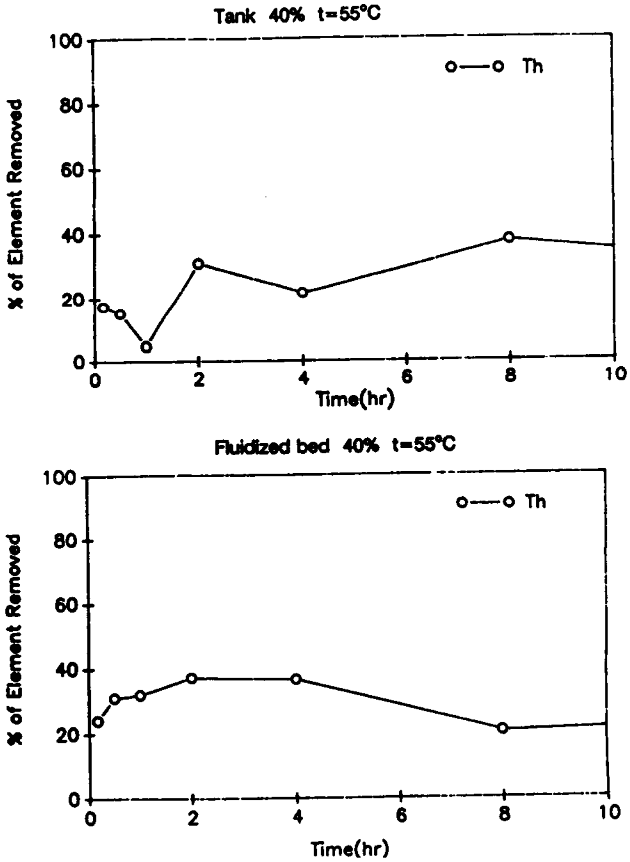

Figure 7. Removal of Thorium.

The radioactive isotopes of thorium, uranium, bismuth, and radium are present in varying amounts in different geothermal residual sludges. Depending on the isotopes, the activities vary from 9 x 10^{-11} to 2 x 10^{-10} Ci/g. These levels of activity require very careful sample preparation and calibration. Further, while for the long-lived isotopes, i.e., those of uranium, lead, and thorium, ICP-MS is calibrated and can be used under the existing environmental guidelines. In order to comply with safety requirements, radium has to be counted. A collaborative effort with BNL's Health Physics, Safety and Environmental Department, is now underway in developing routine analytical protocols for these analyses. This is of paramount importance because if regulatory requirements expect that the radionuclides concentration, say of radium, be in the order of picocuries, i.e., 10^{-12} Ci/g, then extreme care in measurements must be maintained, particularly since at such low levels, 30%-50%, errors can easily be introduced, resulting in difficult, if not impossible, interpretation of results.

Detailed Analysis of Process Variables

Studies of process variables have shown that the overall biochemical waste treatment process is highly sensitive to conditions used. In view of this, systematic studies of each variable have been initiated. We wish to report preliminary results which describe the effect of sludge loading on the capital and operating costs. The effects of different sludge loads in the reactor on the consumption of bacteria, flow rates, neutralization, reinjection of liquids, and quantity of regulated concentrate are tabulated in Table 1.

Table 1

The effect of loading variable on the Biotreatment Process at 55°C and a 4 hr cycle.

Solids Loading in Reactor (%)	Stream No. (lb/h)					Sol. Salts in Rx Mixture (%)
	2	4	8	9	10	
10	16691	36680	120	15318	1494	3.1
20	8345	20007	53.5	7751	648	5.5
30	5564	14450	32.1	5216	379	7.4
40	4173	11670	21.9	3942	252	9.0

*Stream numbers refer to Fig. 3. Results reported in Table 1 represent an example of how just a single variable influences the overall process.

Thus, an increase in the loading of solids in the bioreactor will:

1. Decrease the consumption of bacterial culture (stream 2).
2. Decrease the flow rate at the reactor exit (stream 4).
3. Decrease the consumption of calcium hydroxide (stream 8).
4. Decrease the quantity of reinjection fluid (stream 9).
5. Decrease the quality of regulated concentrate (stream 10).
6. Increase the concentration of soluble salts (KCl + NaCl) in the reaction medium.

Therefore, an increase in the loading of solids in the bioreactor will also reduce the capital and operating costs. Likewise these results also suggest that an increase in the soluble salts in the reaction mixture allows bacteria to be grown in the working salt solution. Other key process variables such as volume of reactor, quantity of regulated material, continuous vs. batch processes, types of bioreactors/different types of filters, etc., are now being systematically investigated. While these studies are time-consuming, they are critical as evidenced by preliminary results which make it possible to consider the topics discussed in the next section.

Sampling Analyses and Waste Disposal Costs

For the purpose of this discussion the following example will be considered first. The El Centro site in California, contains a relatively small volume of wastes. Extensive chemical characterization of this site has been carried out (see, Bechtel Report 1991). Samples taken for analyses were by and large diluted 50:50 with sand. Practically speaking, such diluted samples fall within the regulatory limits as shown in Table 2, and the "dilution approach" may be applicable in some cases and under certain conditions. However, large volumes of waste, for example 5000 lb/h, such as those discussed in this paper would require doubling or more in waste volume, which at best will have disposal and/or storage limitations. Further, if regulatory limit for, say, total α radioactivity is set, for example, at 15 pci/g, then without taking the particulate and aerosol effects into consideration, even diluted samples would be over allowable limits.

Table 2

Selected Analyses of El Centro Samples.
CAL-WET RESULTS
(Citrate Leaching)*

Sample	metal, ppm (Arsenic)**		Radioactivity*** (pCi/g (Totalα)	
	50:50 dilution	no-dilution (estimated)	50:50 dilution	no dilution (estimated)
TP-A4	4.3	8.6	11	22
BP-A5	7.5	15.0	14	28
BP-B5	2.5	5.0	67	134
BP-C3	5.0	10.0	72	144

* Field Investigation Report
Bechtel Environmental, Inc., Nov. 1991
** Limit 5 ppm
*** Limit 15 pCi/g

In 1985, the graded cost for type II-I disposal was $200.00 per ton and $75.00 per ton for non-hazardous waste.[8] The non-hazardous waste was defined as that not exceeding the total threshold limit concentration (TTLC) and soluble threshold limit concentration (STLC). Examples in Table 3 show the regulatory concentrations and those after the biotreatment (Biot).

Table 3

Comparison of regulatory concentration for copper and chromium.

Metal	STLC mg/L	(Biot) mg/L*	TTLC mg/kg	(Biot) mg/kg
Chromium VI Compounds	5	0.25**	500	100
Chromium III Compounds	560	28**	2500	500
Copper Compounds	25	0.25	2500	500

* Based on metal recovery.
** Based on total chromium compounds.

An 80% removal of the metals represents a 60% savings. It is to be understood, however, that the cost of disposal and long term liabilities are continuously increasing while the available space for disposal is diminishing. For example, at BNL disposal of a similar sludge cost $500.00 per ton in 1991. The corresponding non-regulated waste disposal cost was $100.00 per ton. If the sludge contains in addition to chromium and lead, say radium, then it has to be shipped at a cost of $400.00 <u>per cubic foot</u>. On the other hand, removal of the metals leaving radium alone produces waste costing $76.00 per cubic foot to dispose of or $10,800 and $2052 per ton respectively, representing a five-fold saving already achievable on a laboratory scale.

Accepting the fact that disposal costs vary with location, time, local circumstances, etc., the above costs when combined with the very preliminary process costs estimates discussed earlier in this paper, present a cost/benefit scenario given in Table 4.

Table 4

Biochemical Treatment Plant Costs Vs. Costs of Treated and Untreated Waste Disposal.

Quantity of geothermal sludge to be treated: 5130 lb/hr
Working hours per year: 8000 hr
Total capital cost + start up: $4,209,000
(Purchased equipment cost: $518,000)

	1985	1991
Waste Disposal Cost:		
for non-regulated waste ($/ton)	75	100
for regulated waste ($/ton)	200	500
Annual Total Expenses ($): untreated geothermal sludge disposed of directly	4,104,000	10,260,000
Geothermal Sludge Treated:		
by the bio-chemical process (non-regulated waste disposal cost)	1,539,000	2,052,000
waste concentrate (regulated disposal cost)	202,000	504,000
operating costs, etc.	1,396,000	1,396,000
Amortized Payment (fixed)	685,000	685,000

CONCLUSIONS

The geothermal residual sludge detoxification biotechnology R&D phase described in this work allows the following conclusions:

1. Fast detoxification rates are achievable.

2. Cost effective processes(es) operate at elevated temperatures and acidic media.

3. Consistent results indicate that toxic metals are removed in the early phases of the treatment.

4. Forty percent sludge loadings can be achieved.

5. Process cycles of 24h are routine. Preliminary results also indicate that 4 to 10 hour cycles are achievable.

6. Specific combinations of microbial organisms are highly advantageous, particularly in the removal of radioactive isotopes.

7. Increase in the loading of geothermal solids in the bioreactor reduces the capital and operating costs.

8. Current data indicate that with further modifications, an efficient removal of radioactive isotopes (thorium, uranium, radium) is also achievable.

9. The bioprocessed wastes will ultimately be disposed of as non-regulated wastes.

ACKNOWLEDGMENTS

This work has been supported by the U.S. Department of Energy, Department of Energy Conservation, Division of Geothermal Technology, under Contract No. AM-35-10. We wish to acknowledge the valuable help and assistance of L. Racaniello, BNL, for the development and maintenance of microbial cultures used in these studies. We also wish to acknowledge G.K. Ji, for analytical work performed in this program.

REFERENCES

1. Premuzic, E.T. and Lin, M., "Developments in Geothermal Waste Treatment Biotechnology", <u>Geothermal Program Review VII</u>, U.S. DOE CONF-890352, pp. 77-81, March 1989, San Francisco, CA.

2. Premuzic, E.T. and Lin, M., "The Role of Biotechnology in the Treatment of Geothermal Residual Sludges", <u>Seventh International Heavy Metals in the Environment Conference</u>, Geneva, Ed. J.P. Vernet, Pub. CEP Consultants, Vol 2, pp. 60-63, Sept. 1989, Edinburgh, UK.

3. Premuzic, E.T., Lin, M.S., and Kang, S.K., "Advances in Geothermal Waste Treatment Biotechnology", <u>Geothermal Program Review IX</u>, U.S. DOE CONF-S18105, pp. 77-84, March 1991, San Francisco, CA.

4. Premuzic, E.T., Lin, M.S., and Kang, S.K., "Progress in Geothermal Waste Treatment Biotechnology", Geothermal Resources Council, Transactions, Vol. 15, pp. 149-154, 1991.

5. Premuzic, E.T. and Lin. M.S., "Geothermal Waste Treatment Biotechnology, International Conference Heavy Metals in the Environment, Ed. J.G. Farmer, Pub. CEP Consultants, Vol. 2, pp. 95-98, 1991, Edinburgh, UK.

6. Premuzic, E.T. and Lin, M., "Analysis of the Residual Sludge from the Salton Sea Scientific Drilling Project", BNL-42274, 1989.

7. Premuzic, E.T., Lin, M.S., and Ji, G.K., "Applications of Induced Coupled Plasma Mass Spectrometry (ICP-MS) in the Analysis of Geothermal Residues and Chemically Related Materials", in preparation, 1992.

8. Dobryn, D.G., Brisson, A.L., Lee, C.M., and Roll, S.M., "Bioleaching of Toxic Metals from Geothermal Waste", A Preliminary Engineering Analysis, BNL 38523, 1986.

Geothermal Brine Chemistry Modeling Program

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ABSTRACT

The UCSD brine chemistry program is providing highly accurate models of the behavior of high temperature brines to be used by the geothermal community to optimize production, interpret formation behavior and assist in performance assessment. Models are now available as user-oriented programs packaged for both main frame and personal computers (IBM and Macintosh). A manual describing the models and their application to various geothermal problems has been developed and made available to potential users. Tutorial sessions have been held and future sessions are planned.

Present models can be used to predict the behavior of many important geothermal processes. For example, the tendency for production fluids to form carbonate, silica and sulphate scales can be predicted as a function of brine composition, temperature and CO_2 partial pressure. The breakout pressure (onset of two phase flow) can be calculated as a function of temperature and brine composition. Preliminary models are available for characterizing H_2S gas/liquid distributions and the acid-base properties of the $H_2S - H_2O$ system as a function of brine composition, temperature and pressure.

For the past year, a substantial part of our research has focused on the prediction of the properties of gasses in the $CO_2 - CH_4 - H_2O$ system. We have developed highly accurate equations of state for each of the endmembers of the system for a pressure range of 0 to 8000 bar and temperatures from 0 to 1000°C. In order to treat the mixtures of importance to geothermal applications, a mixing model based on the endmembers has been developed. The resulting equation of state for mixtures can be integrated analytically to obtain the free energies and enthalpies of the mixed gasses for a temperature range of 50 to 1000°C and pressures from 0 to 3000 bar. Predictions of this model are within the accuracy of the experimental data and can predict the properties of the liquid phase, the gas phase and the coexistence of these phases with roughly equal accuracy.

Currently, in this program we are also investigating the possibility of predicting the thermodynamic behavior of real gasses from first principles. We have shown that molecular dynamic simulations using simple forms for the interaction potentials produces a PVT relation that is very nearly within the accuracy of the experimental data. The form of the potential used in these calculations implies a two parameter scaling of the equation of state which gives a very efficient representation of the experimental data for all the systems. These results suggest that for many systems sufficiently accurate property estimations may be obtained directly from theoretical calculations.

We have also initiated a program to calculate the enthalpy of brines and gas phases as a function of temperature, pressure and composition. These results may be obtained from our existing models of the free energy and may be used to compute the gas-liquid distributions after brine flash. As they are developed and validated, these models will be incorporated in our package for distribution.

INTRODUCTION

Most geothermal operations are significantly impacted by the chemical problems which result from the handling of geothermal fluids (production, energy removal and disposal). Control of these problems will determine how long these operations can be successfully carried out. Furthermore, it is necessary to minimize the costs of controlling chemical problems in order to make geothermal energy production economically competitive. Consequently, the Department of Energy (DOE) is supporting the UCSD [illegible] n order to provide technology which will help reduce the risks associated with the chemistry of geothermal systems. The thermodynamic models we are developing for predicting the behavior of geothermal brine-solid-gas systems are highly accurate and flexible. In addition, these models summarize, generalize and extrapolate the available thermodynamic data for the brines and gas phases associated with geothermal power production. Thus, they provide an effective and low-cost tool for understanding the complicated chemistry of geothermal brines and for predicting and simulating this behavior. Design engineers and operations experts may reliably use this technology to optimize both the design and operation of geothermal power production systems.

At this time, models which treat a number of problems associated with the development and operation of geothermal power plants are available. They have been validated by extensive comparisons of their predictions with experimental data. The capabilities of the models we have developed to date are summarized in Table 1. Versions of the models have been developed for IBM, Macintosh and main frame computers (e.g., SUN). A manual outlining the development and operation of the models is available. Further model development is briefly reviewed in the following sections.

MODELS OF GAS THERMODYNAMICS

The scaling behavior and other important properties of geothermal fluids are very significantly affected by the presence of dissolved gasses. For example, the contribution of the partial pressures of insoluble gasses dissolved in the brine to the total pressure required to keep a geothermal brine in a single phase condition may exceed the contribution from the vapor pressure of the solvent. In such a situation, the insoluble gas composition will determine the conditions for the formation of two phases (breakout). In other situations (e.g., geopressured systems), an insoluble gas, such as methane, may be one of the energy products of the resource. Models which characterize the solubility of gasses in aqueous solutions and the thermodynamic behavior of gas mixtures are necessary to predict the behavior of such systems. Since transitions from gas to liquid behavior in near critical situations may be of interest, it is desirable to have these models extend continuously from liquid to gas regions.

Many important geothermal gas phase compositions fall within the $CH_4 - CO_2 - H_2O$ system. In last year's report, we discussed equations of state (EOS) that we had developed for

Table 1. PROJECT PROGRESS
CAPABILITIES OF PRESENT MODELS

- Predict Behavior of Calcium Carbonate Scale Formation in NaCl and $CaCl_2$ Brines for T = 0° to 250°C (PC Version Available)
- Predict Solubility of CO_2 and CH_4 in NaCl Brines for T = 0° to 250°C (PC Version Available)
- Predict Solubility of Amorphous Silica Scale in Seawater-Type Brines for T = 0° to 250°C
- Predict Solubilities of Marine Scaling Minerals (NaCl, $CaSO_4$, etc.) to 250°C
- Calculate Dissolution-Solution Characteristics of Rock-Water Systems Containing Na, K, Ca, Cl, and SO_4 for T = 0° to 250°C
- Calculate Dissolution-Solution Characteristics of Rock-Water Systems Containing Na, K, Mg, Cl and SO_4 for T = 0° to 250°C
- Predict Onset of Two Phase Behavior (Breakout) in NaCl Brines
- Predict Solubility of Hydrogen Sulfide (H_2O–H_2S–HS^-) System (preliminary, 0° - 90°C; 0 - 60 atm)
- Predict Partial Fugacity in Mixed Gas System (CO_2–CH_4–H_2O) T = 0° to 1000°C and P = 0 to 1000 bars
- Predict Gas-Liquid Equilibrium in the $CO_2 - CH_4 - H_2O$ system to 1000°C and 3000 bar
- Predict Enthalpies of Brines (preliminary, 0° - 250°C) and Gasses (preliminary, 0° - 1000°C)

the end members in this system. We showed that an equation can be developed that predicts PVT behavior within experimental accuracy for a range of pressure from 0 to 8000 bar and a range of temperature from 0 to 1000 °C. This equation had the form:

$$Z = 1 + \frac{BV_r}{V} + \frac{CV_r^2}{V^2} + \frac{DV_r^4}{V^4} + \frac{EV_r^5}{V^5} + \frac{FV_r^2}{V^2}\left(\beta + \frac{\gamma V_r^2}{V^2}\right)\exp\left(-\frac{\gamma V_r^2}{V^2}\right), \quad (1)$$

where B, C, D, E, F are functions of temperature. For a description of this equation, see our recent publication (Duan et al., 1992a). In order to obtain an equation of state for mixtures, it is common to extrapolate the single component behavior to mixed systems by assuming that the parameters in the EOS at constant temperature and pressure (e.g., B, C, D, etc.) are a function of the composition of the mixture. The equations (called mixing rules) chosen to describe the composition variation must return the parameter values for the end member systems. Beyond this condition, however, there is very little guidance as to the form that the mixing equations should take.

In the prior report, we discussed a set of mixing equations we developed which provides adequate representation of the data that we were able to obtain. However, while the agreement with the data is very satisfactory, there are several problems with these equations. The most important is that the mixing rules themselves are functions of pressure and therefore are not consistent with Eq.(1) when viewed as an expansion in the inverse volume. This means that Eq.(1) when applied to a mixture is not easily integrated to obtain other thermodynamic functions such as the free energy. Since the free energy is required to predict phase behavior, it is an essential property for geothermal applications. In order to provide a more useful representation of the data, we investigated an alternative form for the mixing equations which is loosely based on the virial expansion. In this form, the coefficients in Eq.(1) (B, C, etc.) are expressed as simple products according to the order of the density or inverse volume dependence of the appropriate term in Eq.(1). For example,

$$B = \sum_i\sum_j x_i x_j B_{ij} \quad \text{and} \qquad (2a)$$

$$C = \sum_i\sum_j\sum_k x_i x_j x_k C_{ijk} \qquad (2b)$$

These equations and the method of evaluation of the parameters in Eq.(2) are explained in more detail in our recent publication (Duan et al., 1992b). The accuracy of the equations of state generated in this way is roughly equivalent to that of the earlier equation. However, this new equation of state may now be analytically integrated to give the free energy, enthalpy, etc.

We found that the above equations can describe both the PVT relations and the phase equilibrium properties of gas mixtures nearly within experimental accuracy. An example of the application of the new EOS to the prediction of liquid/vapor coexistence as a function of pressure and CO_2 composition for the important $CO_2 - H_2O$ system is given in Fig. 1. Note that the model is accurate for large ranges of temperature and pressure.

FIRST PRINCIPLE PREDICTION OF PVT PROPERTIES

The values of the parameters in Eq.(1) are determined from a large experimental data base. For many pressure and temperature ranges an adequate data base does not exist. This is particularly true for mixtures. For example, there are essentially no ternary data in the $CH_4 - CO_2 - H_2O$ system. For this reason, we have initiated a program of direct simulation of PVT properties from first principles. Assuming the interactions between particles can be described by a simple Lennard-Jones potential, the motion for a representative system of particles may be calculated by integration of Newton's equations of motion on a fast computer. By averaging over the simulated trajectories, the pressure and temperature may be calculated for a given energy and volume. We have carried out such a simulation with CH_4 as a representative gas system. Comparisons of simulated results with experimental values are given in Table 2. Remarkably, the result of these first principle simulations are within experimental accuracy for a very large range of temperatures and pressures. By fitting the results for extensive simulations of CH_4 and the available experimental data (Duan, Mϕller and Weare, 1992a), we have obtained an equation of the form of Eq.(1), which is a function of the volume and temperature. This equation now fits the simulated and measured data for a range of pressures from 0 to 20,000 bar and temperatures from 0 to 2000° C.

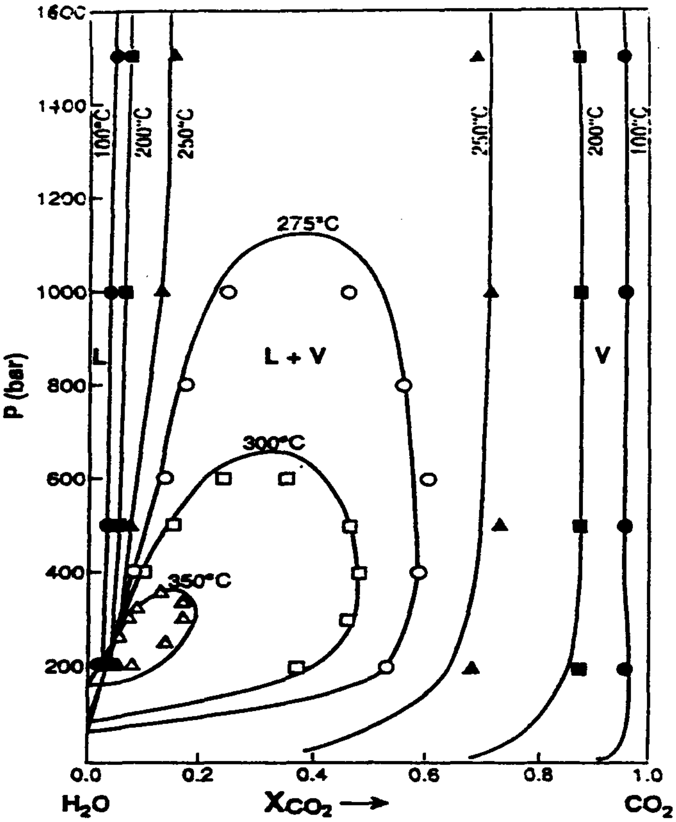

Fig. 1. Liquid-vapor equilibrium in the system, CO_2–H_2O, as a function of pressure and CO_2 composition. The symbols are the experimental data of Todheide *et al.* (1963).

Because of the form of the potential chosen, the PVT simulations of a single gas can be generalized to another by simple scaling. The equation may be generalized to treat other systems as follows. We scale the temperature, pressure and volume as $P_* = 7996.3\frac{P}{\varepsilon\sigma^3}$, $T_* = \frac{159.02}{\varepsilon}T$ and $V_* = (\frac{3.691}{\sigma})^3 V$, where σ, and ε are Lennard-Jones parameters for the particular gas. Values of these parameters are available for many species. When L-J parameters are unavailable, they are easily evaluated using relatively few (< 20) PVT data. Now this equation will predict the PVT properties of many other systems, such as CO_2, N_2, CO, Cl_2, O_2, H_2. Results of such calculations (see Table 3) indicate that for many systems extensive measurements may be replaced by simulations. Because of the paucity of data for many gas systems, this technology is important to meeting the DOE goal of being able to accurately predict the thermodynamics of geothermal gas-brine systems. We are expanding these simulations to include mixtures and a wider range of compositions. Results for the end member systems have been summarized and will be submitted for publication.

ENTHALPY PREDICTIONS

This year we began a program to expand our calculations to include other thermodynamic properties of interest to the geothermal community with the general objective of producing a complete equation of state as a function of T, P and composition for geothermal brines and the associated gas phases. One of the most important of these calculations is the enthalpy of the gas and liquid phases.

Table 2. A Comparison of Molecular Dynamics Simulated PVT Properties with EOS * Calculated Values

T(°K)	P(bar)	V(cm³*)	V (cm³, MD)	T(°K)	P(bar)	V(cm³*)	V (cm³, MD)
223.9	40.9		360.00	550.0	2064.0	49.88	50.00
575.3	135.7	362.39	360.00	1107.0	4604.0	49.71	50.00
849.1	748.0	119.36	120.00	228.2	1101.0	39.49	40.00
1034.1	918.0	120.64	120.00	251.0	1288.3	40.16	40.00
1251.1	1141.0	119.53	120.00	284.1	1689.0	39.94	40.00
302.0	350.0	69.90	70.00	228.0	2277.0	34.54	35.00
508.0	877.0	70.23	70.00	334.0	3721.0	35.12	35.00
1376.0	2885.0	69.90	70.00	674.0	7355.0	34.98	35.00
445.0	955.0	60.92	60.00	238.0	5483.0	29.78	30.00
855.0	2303.0	59.89	60.00	337.0	7583.0	30.04	30.00
1005.0	2796.0	59.51	60.00	369.0	8196.0	29.97	30.00
1178.0	3295.0	59.76	60.00	406.0	8788.0	29.95	30.00
1390.0	3911.0	59.90	60.00	457.0	9747.0	29.77	30.00

* The volume calculated from the equation of state (EOS) of (Duan *et al.*, 1992a). This equation of state is within experimental error (0.466% comparing with 1083 data points).

Since in the brine models we calculate the free energy as a function of temperature, the enthalpy may be calculated from the derivative,

$$\left\{\frac{\partial\,(\Delta G/T)}{\partial\,T}\right\}_P = -\frac{\Delta H}{T^2} \qquad (3)$$

Our modeling approach for describing the free energy as a function of temperature has been discussed in several publications (see, for example, MΦller, 1988). Fig. 2 compares the enthalpy of aqueous NaCl solutions calculated by our model (MΦller, 1988) with values determined by the extensive correlation of Pitzer *et al.* (1984). Note that the binary parameters for the NaCl system were evaluated by fitting both heat and free energy data (MΦller, 1988; Pitzer et al., 1984). This is often the case for the binary parameters (MΦller, 1988; Greenberg and MΦller, 1989). However, many of the mixing parameters and all of the parameters for the slightly soluble salts were determined from free energy data alone. In these cases, when the free energy is differentiated in Eq.(3) there may be an increased error. We will be testing enthalpy calculations for other systems against available data in the near future.

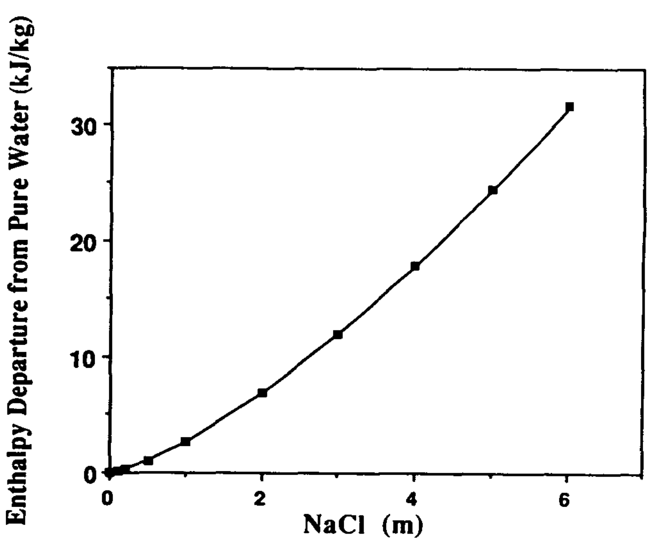

Fig. 2. A comparison of model calculations (solid line) of the enthalpy of aqueous sodium chloride solutions as a function of concentration with values (solid squares) fit by the extensive correlation of Pitzer *et al.* (1984).

Table 3. A Comparison of PVT Properties Computed Using Eq. (1) with the Experimental Data

T(°K)	P(bar)	V(cm^3, Eq.(1))	V_{exp} (cm^3)	error%	ref*.
CO_2					
1073.15	25.00	3640.01	3607.40	0.9038	Michels et al. 1934
573.15	100.00	466.02	462.78	0.7004	-
1073.15	100.00	924.17	909.30	1.6358	-
373.15	1000.00	45.43	44.77	1.4782	-
1073.15	1000.00	113.37	114.13	-0.6636	-
373.15	2000.00	39.22	38.70	1.3335	Juza et al., 1965
573.15	2000.00	48.85	48.93	-0.1683	-
973.15	8000.00	38.37	37.81	1.4824	-
N_2					
373.15	379.43	99.97	99.93	0.0415	Michels et al., 1936
373.15	2602.11	39.16	38.65	1.3205	-
453.15	1519.88	51.82	51.60	0.4314	Tsiklis. Polykov, 1968
473.15	7092.75	30.64	30.44	0.6716	-
673.15	1519.88	64.64	65.67	-1.1820	-
673.15	7599.38	32.98	32.95	0.0904	-
H_2					
373.15	5000.00	19.77	20.21	-2.1957	Tsiklis et al., 1975
373.15	6000.00	18.85	18.75	0.5453	-
423.15	6000.00	19.43	19.70	-1.3803	-
423.15	7000.00	18.68	18.17	2.7866	-
Cl_2					
550.15	10.00	4512.10	4497.00	0.3358	Angus et al.,1978
550.15	250.00	117.46	118.40	-0.7958	-
900.15	100.00	737.88	737.90	-0.0030	-
900.15	250.00	291.15	291.80	-0.2236	-
O_2					
473.15	5066.00	29.32	29.26	0.1880	Tsiklis et al, 1965
473.15	7092.00	26.57	26.78	-0.7919	-
407.10	4049.20	30.17	30.00	0.5777	-
1193.80	17037.20	25.73	25.00	2.9269	-
CO					
473.15	5000.00	34.14	34.32	-0.5251	Robertson. Babb, 1968
473.15	10000.00	28.13	28.05	0.2985	-
573.15	10000.00	29.29	29.09	0.7000	-

* See References

In Fig. 3 we compare our model calculations of the enthalpy of the highly concentrated Salton Sea geothermal brine with that of pure water as a function of temperature. We note a difference of approximately 15%. This would create an error of similar magnitude in gas/liquid partitioning calculations which are an important geothermal application of enthalpy estimates. For example, in the constant enthalpy flash of a geothermal fluid from 300°C to 100°C, the error in the gas/liquid ratio would be about 20%.

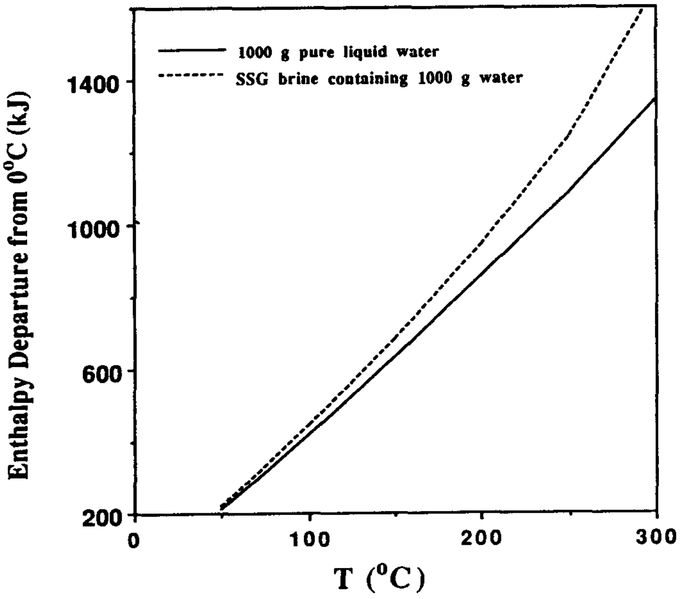

Fig. 3. A comparison of model calculations of the enthalpy of pure water (solid line) and of the enthalpy of a concentrated geothermal brine (dashed line, Salton Sea) as a function of temperature.

The situation for gas phase models is somewhat different. In this case, we have an equation of state for the system as a function of volume. Integrating this equation gives the appropriate equation for the enthalpy as,

$$\frac{\Delta H}{RT} = Z - 1 + \frac{2a_2 + 3a_3/T_r}{V_r} + \frac{2a_5 + 3a_6/T_r}{2V_r^2} + \frac{2a_8 + 3a_9/T_r}{4V_r^4} + \frac{2a_{11} + 3a_{12}/T_r}{5V_r^5} + \tag{4}$$

$$3\frac{a_{13}}{2\gamma T_r^3}(\beta + 1 - (\beta + 1 + \frac{\gamma}{V_r^2}) \exp(-\frac{\gamma}{V_r^2}).$$

Using Eq. (1) for the pure water (solid line) system and for the H_2O–CO_2 (dashed line) mixed system, we obtain the results represented in Fig. 4 for the variation of enthalpy with pressure at T=200°C. Note that at this temperature the system undergoes vapor to liquid transition at P = 15.7 bar. Eq. (1) is essentially based on an ideal gas standard. Yet, as shown in Fig. 4, it gives fairly reliable results even for the latent heat. We note that for most geothermal systems the concentration of CO_2 in the liquid is very small. Fig. 4 shows that the enthalpy of the these solutions would be very nearly the same as that of the gas-free brine. In systems with low gas content, it may be more accurate to use the brine enthalpy as calculated in Eq. (3).

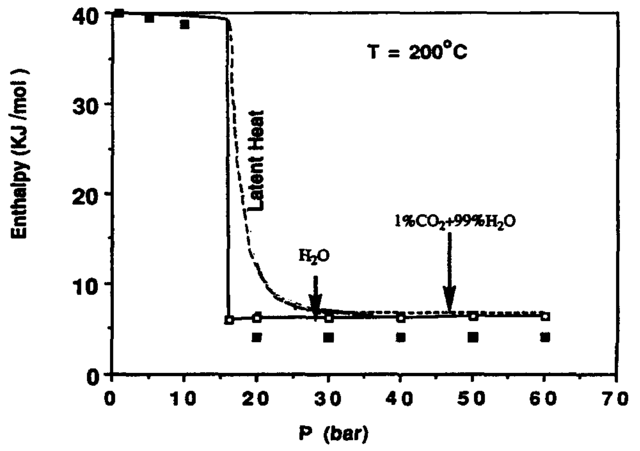

Fig. 4. A comparison of model calculations (using Eq. 1) of the variation with pressure of the enthalpy of pure water (solid line) and of the enthalpy of a H_2O-CO_2 mixture (dashed line). The solid squares are experimental data (Haar *et al.*, 1984) for pure water enthalpies.

APPLICATION: PREDICTION OF BOILING DEPTH OF GEOTHERMAL RESERVOIR

As we saw in the above example, the presence of a small amount of CO_2 in a geothermal fluid does not significantly affect the enthalpy of the liquid state. However, the pressure at which the brine enters the two phase region at a particular temperature is significantly affected. This of course determines the depth at which the brine boils in the formation. The following application of our models to scaling in the Steam Boat Geothermal Reservoir in Nevada illustrates this effect. The composition of the fluid is that of the W-235 Well (data supplied by Ted De Rocher, Yankee/Caithness). The fluids in this system contain an average of 3183 ppm CO_2. The temperature (solid line) and pressure profiles (dashed line) measured in the field are shown in Fig. 5. The breakout pressure calculated from our model is also plotted on the figure (dotted line). The fluid will boil when the vapor pressure of the fluid mixture is higher than the confining pressure. In this case, this occurs where the dashed and dotted lines intersect giving a boiling depth of approximately 2300 feet with a corresponding temperature and pressure of 192°C and 22 bar, respectively. This point is important since at breakout the CO_2 is preferentially removed from the fluid leading to significant supersaturation of the brine with respect to calcite. The composition of the vapor phase at breakout for a downhole temperature of 192°C is illustrated in Fig. 6 (point A). The composition of the vapor phase released (given by the solid line in the figure) is rich in CO_2 although there is a considerable amount of H_2O also in the vapor. As the pressure is lowered, the vapor becomes increasingly rich in H_2O and the fluid becomes more concentrated. This of course leads to a rapid supersaturation with respect to calcite and eventually to the precipitation of carbonate scale. We note in Fig. 5, however, that the predicted point of breakout does not coincide exactly with the appearance of scale (indicated by the asterisk) in the well bore.

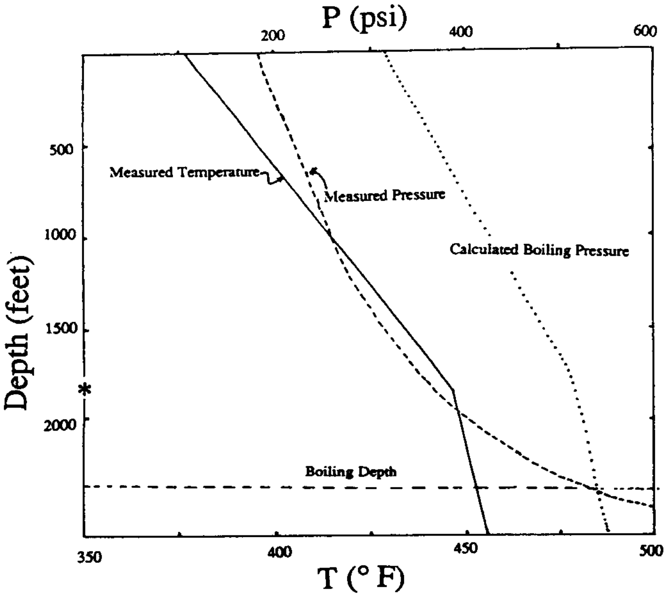

Fig. 5. The prediction of the boiling depth of a geothermal reservoir using field measurements of downhole pressures (dashed line) and boiling pressures calculated with our EOS (dotted line). The fluids from this reservoir (Well 235-G, Steam Boat Geothermal Reservoir, Nevada) contain on the average 3183 ppm of carbon dioxide. The temperature profile measured in the field is shown by the solid line. It can be seen (see text) that the boiling depth (horizontal dashed line), where the measured pressure is equal to the calculated boiling pressure, is about 2300 feet and the corresponding downhole temperature is about 192°C. The depth where calcite scale formation is observed is indicated by the asterisk.

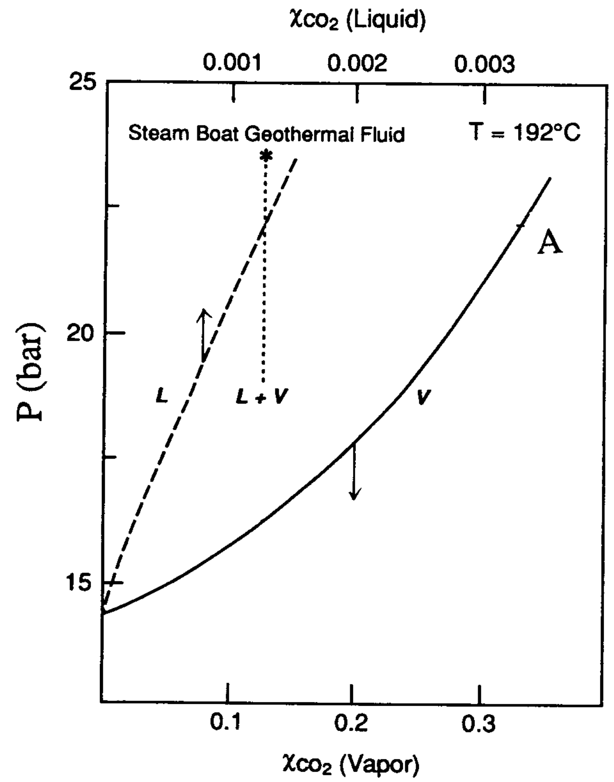

Fig. 6. Model calculations of the variation of CO_2 content in the brine (Well 235-G, Steam Boat Geothermal Reservoir) and in the vapor phase released (solid line) as a function of pressure. For a breakout temperature and pressure of 192°C and 22 bar, respectively, (see text) the composition of the vapor phase at breakout is indicated by point A.

In order to understand this discrepancy better we investigated how the supersaturation changes with depth in the well with the following model calculations. The SBGR brine was equilibrated with calcite at bottomhole formation conditions. Then, the resulting brine was gradually brought to surface conditions. Above 2300 ft, the calculated vapor pressure of the brine exceeded the pressure of the formation (see Fig. 5) and the system changed from one phase into two phases. The gas phase released has a relatively high concentration of CO_2 while the liquid phase is gradually depleted in CO_2. The pressure is further reduced as the fluid moves up the well bore to surface conditions. The reduction in CO_2 and the loss of H_2O as steam leads to supersaturation with respect to calcite as shown in Fig. 7. (Supersaturation is defined as log SR $=\prod_i \frac{a_i^{v_i}}{K_{sp}}$.) Generally minerals will not precipitate until the fluid has reached significant supersaturation levels. However, at some point (usually SR ≈ 10) the calcite spontaneously precipitates as scale. The depth of scale formation observed in the well bore is shown by the cross in Fig. 7. At this depth, our model gives a corresponding SR value of about 12.5, which is entirely consistent with other experience involving calcite supersaturation. These results indicate that our model calculations can give a detailed description of the scale formation process in geothermal wells.

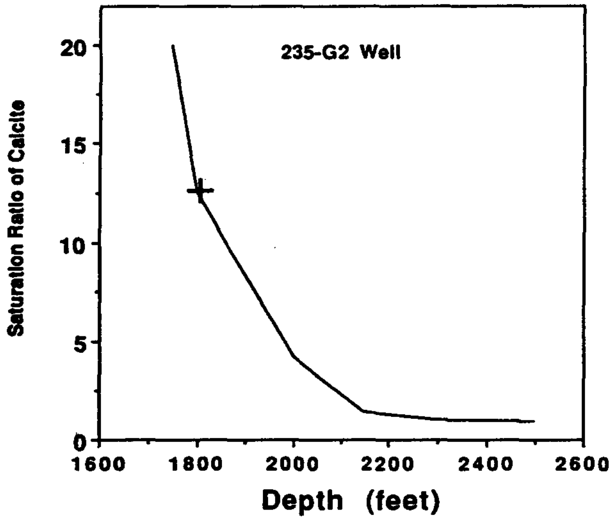

Fig. 7. The calcite saturation ratio predicted as a function of depth in Well 235-G, Steam Boat Geothermal Reservoir. The cross represents the depth at which calcite scale formation is observed.

REFERENCES

Angus, S., Armstrong, B. and De Reuck, K.M. (1985) *International Thermodynamic Tables of the Fluid State 8.*

Duan, Z., Mϕller, N. and Weare, J.H. (1992,a) An equation of state for the CH_4–CO_2–H_2O system: I. pure systems from 0 to 1000°C and from 0 to 8000 bar. *Geochim. Cosmochim. Acta 56* (in press).

Duan, Z., Mϕller, N. and Weare, J.H. (1992,b) An equation of state for the CH_4–CO_2–H_2O system: II. mixtures from 0 to 1000°C and from 0 to 1000 bar. *Geochim. Cosmochim. Acta 56* (in press).

Greenberg, J.P and Mϕller, N. (1989) The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na–K–Ca–Cl–SO_4–H_2O system from 0° to 250°C. *Geochim. Cosmochim. Acta 53*, 2503-2518.

Haar. L., Gallagher, J.S. and Kell, G.S. (1984) *Steam Tables, thermodynamic and transport properties and computer programs for vapor and liquid states of water in SI units.* Hemisphere Publishing Co.

Juza, J., Kmonicek, V. and Sifner, O. (1965) Measurements of the specific volume of carbon dioxide in the range of 700 - 4000 bar and 50 - 475°C. *Physica 31*, 1735 - 1744.

Michels, A., Michels, C. and Wouters, H. (1935) Isotherms of CO_2 between 70 and 3000 atmospheres. *Proc. Roy. Soc. A153*, 214 - 224.

Michels, A., Wouters, H. and Boer, J.D. (1936) Isotherms of nitrogen between 200 and 3000 atm and 0°C and 150°C. *Physica 3*, 585 -589.

Mϕller, N. (1988) The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na-Ca-Cl-SO_4–H_2O system to high temperature and concentration. *Geochim. Cosmochim. Acta 52*, 821-837.

Pitzer, K.S., Peiper, J.C. and Busey, R.H. (1984) Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data 13*, 1-102.

Robertson, S.L. and Babb, S.E. (1970) Isotherms of carbon monoxide to 10kbar and 300°C. *J. Chem. Phys. 53*, 1094 - 1099.

Todheide, K. and Franck, E.U. (1963) Das zweiphasengebiet und die kritische kurve in system kohlendioxide-wasser bis zu drucken von 3500 bar. *Z. Phys. Chem. Neue Folge 37*, 387-401.

Tsiklis, D.S. and Koulikova, A.I. (1965) Oxygen compressibility determination at pressures to 10,000 atm and temperatures to 400°C. (In Russian) *Zh. Phiz. Khimii 39*, 1752 - 1756.

Tsiklis, D.S. and Polyakov, E.V. (1968) Measuring the compressibility of gasses by the displacement method. Nitrogen compressibility at pressures up to 10,000 atm and temperatures to 400°C. (In Russian) *Soviet Physics-Doklady 12*, 904 - 904.

Tsiklis, D.S., Maslennikova, V.Y., Gavrilov, S.D., Egorov, A.N. and Timofeeva, G.V. (1975) Molar volumes and equation of state of molecular hydrogen at high pressures. (In Russian) *Dokl. Akad. Nauk. SSSR 220*, 189 - 191.

Weare, J.H. (1987) Models of mineral solubility in concentrated brines with application to field observations. *Reviews in Mineralogy* (eds., I.S.E. Carmichael and H. Eugster) *17*, 143-176.