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ADDENDUM TO MATERIAL SELECTION GUIDELINES FOR GEOTHERMAL ENERGY UTILIZATION SYSTEMS

Part I: Extension of the Field Experience Data Base
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GEOTHERMAL CHEMICAL CONTROL AND MONITORING INSTRUMENTATION - AN OVERVIEW

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ABSTRACT

We must have accurate knowledge of the geothermal fluid chemistry at operating temperature if we are to optimize operation, prevent corrosion, increase equipment service life and maximize profit and use. Available electrochemical sensors do not survive at the temperatures encountered in geothermal fluids; and new developments in this area are required. In order to fill this gap in technology, the Pacific Northwest Laboratory (PNL) is developing chemical control and monitoring instruments for measuring in situ characteristics of geothermal fluids. Progress in the development of electrochemical sensors to measure pH, carbonate and sulfide-sulfur will be discussed.

INTRODUCTION

Geothermal fluids in the United States are heavily loaded with a variety of chemical species (Table 1) which can accelerate or depress corrosion.[1-6] Several of these chemical species can precipitate in the system causing fouling, decreased flow rates, gas formation, and other undesirable effects. In addition, if the temperature or pressure of a brine changes and is flashed, or outgassing occurs before analysis, the fluid composition can drastically change. Compounds that precipitate are usually found as scales and may not show up as a major component in solution. Common precipitates which remove chemical species from solution include calcium carbonate, silica, barium compounds, basic iron chloride and metallic sulfides. Thus, it is desirable, if not necessary, to use chemical sensors installed in geothermal wells or power systems to obtain accurate information concerning the in situ chemistry of the fluid. Available electrochemical sensors do not survive at the temperatures encountered in geothermal fluids and new developments in this area are required. In order to fill this gap in technology, reduce the risk, and develop the incentives for the commercial sector to meet the need, the Pacific Northwest Laboratory (PNL) operated by Battelle Memorial Institute for the U.S. Department of Energy (DOE) has embarked upon a program to develop sensors for measuring various ionic species and corrosion related in situ characteristics of geothermal fluids. The mission of the work is to develop field tested electrical and electrochemical sensors and test apparatus for in situ characterization of geothermal fluids and to transfer this technology so that the user needs can be met.

TABLE 1. Typical Geothermal Brine Compositions

Species	Range, ppm	Maximum, ppm
Total Dissolved Solids	1,000 - 10,000	360,000
Chloride	100 - 1,000	260,000
Sodium	100 - 1,000	87,000
Sulfate	50 - 500	84,000
Calcium	10 - 100	65,000
Magnesium	1 - 10	40,000
Potassium	50 - 140	30,000
Aluminum	0.5 - 5	7,200
Iron	1 - 10	4,600
Silica	50 - 500	1,060
Ammonium	0.5 - 5	1,050
Nitrate	Not estimated	1,020
Carbon Dioxide	0.5 - 5	500
Lead	0.5 - 5	100
Hydrogen Sulfide	Not estimated	75
Silver	Not estimated	2

BACKGROUND

Geothermal Energy Systems

Geothermal systems may be classified into two categories according to the physical state of the pressure controlling phase.[2] The first and most common are hot water systems, where liquid water is the continuous pressure controlling fluid phase; vapor may be generated as discrete bubbles as the pressure drops, but generally the temperature is so low that liquid predominates. A few geothermal systems, including Larderello (Italy), Matsukawa (Japan), Cerro Prieto (Mexico), the Geysers (California),

and the Hawaiian areas (under development) are in the second category, characterized by dry, superheated steam with little or no associated liquid.

Because of these differences, two types of power generating equipment are used. Where dry steam is available, condensing steam turbines are normally used. The system is very similar to that used in conventional power plants, and works reasonably well if the steam is of good quality, has a relatively small permanent gas content, and is relatively noncorrosive.

The vapor-turbine cycle has been developed to reduce or eliminate the inherent disadvantages where corrosive steam or liquid-dominated systems are found. In this process, the hot water is brought to the surface at sufficient pressure to maintain it as a liquid and is passed through a series of heat exchangers where the heat is transferred to boil and superheat a high density vapor. This vapor is then expanded through a turbine to produce power and then flows to another heat exchanger where it is cooled and returned to the boiler. Practical and economic advantages of this process are believed to be significant because the largest share of the United States (and world) geothermal resources is in systems which have temperatures below 200°C (392 F).

A variety of working fluids can be used in the vapor-turbine power cycle. Isobutane is a working fluid with the right thermodynamic characteristics and promising economics for power generation in binary cycle systems operating below 163°C (325°F). Freon and propane can be used at lower temperatures. The working fluid usually does not cause a corrosion problem, but the primary geothermal liquids can cause severe corrosion and scaling. Unwanted flashing and premature gassing also affect system performance and heat transfer.

We must have accurate knowledge of the geothermal fluid chemistry at operating temperatures if we are to optimize operation, prevent corrosion, increase equipment service life, and maximize profit and use. An alternative to sampling with its inherent problems is instrumentation, which can measure the various chemical species and physical properties of geothermal fluids. Electrochemical sensors, which are available, do not survive at the temperatures encountered in geothermal fluids and others are needed.

Another important use of these sensors is their ability to sense real time changes in the system chemistry and thus provide information that can be used to prevent catastrophic failure. Several examples exist[8] where these sensors sensed butane leaks or changes in chemical composition of fluids at the Magma Corporation's Megawatt Power Plant at East Mesa California prior to unexpected plant shutdown. Repairs and shutdown time resulting from the catastrophic nature of the failure could have been reduced substantially by early use of the information provided by the sensors. The net savings resulting from early detection of a problem, and the reduction in the repairs required, are substantial and will pay for the instrument development effort.[9]

SENSOR DEVELOPMENTS

Some specific sensors and equipment needed for measuring chemical and other factors affecting corrosion, scale formation, identifying abnormalities which affect performance and gassing in geothermal fluids, were identified in the NMAB report, and the priority for their development was tentatively outlined.[7] These priorities were further refined by personnel in the United States Department of Energy and PNL to identify and establish development projects to be conducted both in-house and by contract-research external to the laboratory. Tables 2 and 3 list instruments being developed.

TABLE 2. PNL Projects

Sensor	Status
Reference Electrode	Field Testing
Conductivity Cell	Field Testing
Scaling Rate Meter	Designed, not tested
Redox Probe	Field Testing
Corrosion Rate Meter	Field Testing

TABLE 3. Contracted Projects

Contractor	Sensor	Status
General Electric Company	pH Sensor (glass)	Field testing initiated
Leeds and Northrup	pH Sensor (glass)	Field testing initiated
Owens-Illinois	pH Sensor (glass)	Laboratory testing complete
Leeds and Northrup	CO_2 Sensor	Laboratory testing underway
Beckman Instruments	Sulfide Ion	Discontinued
University of Pennsylvania	Chem. Sensitive Semiconductor Devices	Development underway

Pacific Northwest Laboratory Developments

The sensors discussed in this subsection were developed at PNL to meet the needs for measuring in situ properties of geothermal fluids. All devices have been field tested to ensure that they will perform as expected in the required application. The field test program will be discussed briefly in a later section.

Reference Electrode

The function of reference electrode is to maintain a constant potential at each temperature so that the potential of other electrode devices can be referred to it. Any change in potential between the two electrodes is then due to the other electrode, rather than the reference electrode, and would indicate some change in chemical environment. For example, change in pH and/or the concentration of a specific ion would

be indicated by a potential difference between reference electrode and the pH and/or specific ion electrode. No reference electrode had been designed for use in the highly contaminated hot geothermal environment until PNL completed their design. This design is based on a silver chloride electrode protected by a salt bridge. The unique feature of this design is that the electrode operates at high pressure away from the high-temperature geothermal fluid, and at ambient temperature, so that a streaming potential is avoided. A thermal liquid junction potential is formed, but the potential is stable for extended lengths of time when KCl is used as the electrolyte. The system is not disturbed by the geothermal environment, and electrode life at 250°C is expected to be measured in weeks. This electrode has been completely laboratory-tested throughout the temperature and pressure range expected in geothermal systems (250 to 300°C at pressures of 5000 psi). This electrode is referenced on the Standard Hydrogen Electrode Scale. Major advantages are: carbon dioxide does not interfere with the electrode; its response is independent of the chemical species in geothermal fluids; and it is not affected by hydrogen sulfide, the major component of geothermal systems, which would give a significant reaction. Field tests have been underway since 1978, and the sensor should be commercially available when several of the other chemical sensors are available. Tests at East Mesa, California, and other locations, indicate that the reference electrode is reliable and rugged.

Conductivity Cell

The solution conductivity is a useful measurement because it can indicate the amount of dissolved solids in a solution or salinity differences from different aquifers (when used in well logging). Continuous monitoring of the conductivity can indicate when changes occur in plant water chemistry, well flow conditions (two-phase flow in the bore hole, earthquakes), scale deposition, piping leakage, or oxygen entering the system. Many of these factors, particularly salinity, scaling, and oxygen content, contribute to corrosion and affect plant operation; therefore, the corrosion and operating engineers find these data are useful.

Two- and four-electrode conductivity cells are available, but are not suitable for geothermal and other contaminated or scale-producing systems because they must make direct contact with the solution to measure its conductivity. Electrodeless models have the advantage that they do not require electrical contact with the solution and will operate where scaling is probable.

The PNL conductivity cell,[13] is the only unit of its kind which is operable in the temperature needed (250°C) for geothermal measurements. Basically, the probe consists of two toroidally-wound coils, one driven by a pulsing dc voltage and the other acting as a receiver. The electromagnetic current from the driven coil is coupled through the solution and induces a current in the receiver coil. Induced current is proportional to the solution conductivity. The electronics associated with the probe are available from commercial manufacturers.

The peak voltage response of the toroidal coil is theoretically independent of temperature, so any change in output will be due to changes in solution conductivity. Initially, ferrite toroids were used, but their curie point--the temperature at which the magnetic properties changed rapidly and disappeared--was about 240°C, too low for this project. Tap core toroids were tested, were found to have a curie point about 250°C, and are now used in all probes. A unique spring-loaded seal permits temperature cycling without leakage of brine into the coil compartment.

These devices have been field tested at East Mesa, California since 1976. Indications are that the conductivity cell works well, and reproducible data can be obtained.

Oxidation Reduction Potential

The redox electrode consists of a bare platinum electrode, whose potential is measured versus a reference electrode. In the past,[14] the redox electrode (also known as Eh) has been used to imply the type of chemistry in marine environments, rivers, etc., since it is assumed to be in equilibrium with the local chemistry. PNL investigated this device because it was hoped it could imply the general type of chemistry in geothermal brines.

In reality, the redox electrode[14] was not found to be a very sensitive indicator of the general chemistry. However, it is extremely sensitive to the presence of oxygen and would make an ideal oxygen detector. Even traces of oxygen result in large increases in corrosion rates of the carbon steel plant components. Consequently, this sensor can easily provide the plant operator with a warning to take preventative actions when oxygen enters.

The redox electrode has been successfully field tested at East Mesa. Brine usually exists in a highly reducing state, but when oxygen enters the system, the redox electrode quickly responds On several occasions, during plant shut down, the redox electrode indicated oxygen had penetrated the heat exchangers, and plant operators were alerted to use a nitrogen purge to keep out the oxygen.

Corrosion Rate Measurements

For economic reasons, geothermal power plants will be predominantly built using carbon steels. In general,[15] corrosion rates of carbon

steels are acceptably low under reducing conditions at elevated temperatures, and can be expected to have a long lifetime. There are conditions under which corrosion rates can become catastrophic; such as, when oxygen enters the system at elevated temperatures. It would be very useful to have corrosion rate measuring instrumentation, which rapidly responds to transient conditions which result in high corrosion rates.

One device useful in measuring corrosion rates is the linear polarization (LP) probe. There are two domestic commercial manufacturers of linear polarization equipment which can measure instantaneous corrosion rates. Probes have two or three electrodes of the same material, (for example, carbon steel) in which one acts as a pseudo-reference electrode while the other two are polarized. The test electrode in polarized 10 to 20 mV versus the pseudo-reference and the measured current is directly proportional to the corrosion rate. Commercial manufacturers' equipment reads out directly in mills per year and makes this measurement automatically at preset times.

Commercial LP equipment has been tested extensively in the field at East Mesa.[8] These probes gave satisfactory life in the cooling water system, and the corrosion results correlate fairly well with the weight loss coupons. However, the commercial probes failed rapidly in the hot brine. It was found that a high electrical resistance was forming between the electrodes and the screw mounting studs inside the brine system. This high resistance caused the probe to read lower and lower corrosion rates, until it was in error by up to a factor of 100. A probe, fabricated by PNL, has given good service for over five months and is continuing. The electrodes on the PNL probe pass through a spring-loaded Teflon[a] seal to preserve electrical continuity in the high-temperature system. The electrode area is the same as the commercial probe, so the standard electronics can still be used.

Even with the improved PNL probe, the linear polarization method suffers some disadvantages for use in geothermal plants. First, the electrodes must stay wet since an electrolyte is needed for the method to work. This means, if the system is drained and air admitted, the very high corrosion that occurs may not be recorded. Attempts were made to avoid this problem by placing the probe in the U-tube water trap; however, in this configuration, the probe is subject to being buried in sand and is not in the main flow stream. This proved to be a problem since we found brine velocity to be very significant in determining how much corrosion occurred.

Electrical Resistance Corrosion Probe

A second device useful in measuring corrosion rate is the electrical resistance corrosion probe. Probes of this type were installed at many locations throughout the plant. The probe incorporates a commercially available, resistance-type corrosion probe and space for Teflon insulated corrosion/scale coupons. As the thin-wall element of the corrosion probe corrodes, its electrical resistance changes and can be converted by calculation to a corrosion rate in units of MPY (0.001 in./yr). The probe includes temperature compensation on the inside for a bridge circuit. Some of the probes used in the plant had only samples and a thermocouple. The commercial unit that was field tested used replaceable electrodes which screw onto a metal stud with a gasket of Nitron or Kalrez[b] in between to keep out the corrosive liquid. After a couple of weeks at 170°C, the gasket leaked, permitting brine to enter the threaded stud region, thus corroding the contacts. This resulted in a highly resistive contact to the electrode, which prevented a useful corrosion rate measurement (the device read low). PNL substituted a new EPDM[a] elastomer, developed for geothermal environments, and the problem has disappeared. The response of these units now agrees with corrosion data found using weight loss coupons placed in geothermal process streams, and the LP method.

CONTRACTED DEVELOPMENTS

Five sensors, and a new class of sensing elements called Chemically Sensitive Semiconductor Devices (CSSD's) are being developed on subcontracts with industrial organizations and universities. The following subsections will discuss each of these sensors. The need for each sensor was identified in the NMAB report and prioritized relative to program requirements.

pH Electrode

The most important variable measured in water chemistry is pH, the relative acidity or alkalinity. Changes in pH affect corrosion, scaling, gas formation and the activity of other ionic species. Corrosion engineers and chemists use in situ and other pH measurements to help them evaluate construction materials and predict materials performance and operating equipment performance. High-temperature glass pH electrodes have been developed and laboratory tested under contract with Owens-Illinois at Toledo, Ohio, and with Leeds and Northrup, Inc., at North Wales, Pennsylvania. We attempted to extend conventional technology to provide devices to operate in geothermal systems at approximately 250°C and 5,000 psi pressure. In addition, the electrode was to be: 1) relatively free of

(a) Trademark of E.I. duPont de Nemours, Inc.
(b) Trademark of L' Gande, Inc.

interferences from ionic species within the geothermal fluid, 2) designed to withstand hazards (fluid hazards, rocks, etc.) for a reasonable time, and 3) compatible with a variety of electrical transmission systems.

Laboratory tests, completed at the contractors' laboratories, showed that the electrodes could survive in a simulated geothermal environment up to 250°C[18,19] and respond to pH changes at temperatures slightly above 200°C. Work to confirm these results, completed at PNL to determine the precision of the electrode(s) response and calibrate these devices, showed that the electrodes could not be used in geothermal service at temperatures above 100°C. Apparently, the pH glass response is effected by the fluid and fails to respond to pH change in a hertzian fashion. Further development in this area was thus abandoned.

A high-temperature zirconia ceramic electrode is also being developed by General Electric Company, Schenectady, New York. Minimum specifications for this device are the same as for the glass pH electrodes. Laboratory testing has shown that this electrode will respond to pH changes in simulated geothermal fluids at 285°C and pressures up to 1200 psi.[20] Laboratory work required to confirm these results at higher pressures, and to identify the life of the device in geothermal fluids, has been completed by the contractor. These devices have been tested at PNL to confirm the contractor's results and provide additional information on the electrodes performance. The electrode responds to pH in a near-hertzian fashion, but is not yet absolutely reliable. Problems are believed to be related to surface flaws in the ceramic zirconia. If this is true, better quality zirconia tubes will solve the problem.

Plans are for the electrodes to be tested in the field in operating geothermal systems this year.

CO_2 Sensor

Carbon dioxide is present in all geothermal fluids. When pressures decrease, carbon dioxide gas is produced, resulting in scaling, pH change and corrosion. In addition, CO_2 evaluation can cause severe loss in turbine and heat exchanger performance unless properly controlled. Corrosion engineers and plant operators need these data to choose construction materials properly, to evaluate equipment life and performance, and to predict upset conditions during operations. Leeds and Northrup, Inc., has designed a CO_2 sensor.

A Stowe-Severinghouse type CO_2 electrode has been designed for this application.[21] This electrochemical approach uses a carefully designed pH and reference electrode combination to measure CO_2 concentration caused by diffusion of CO_2 through the membrane. Compensation for H_2S interference is achieved using a chemical getter located in the diffusion membrane. The technology required to develop this system is closely related to that required to measure CO_2 in more moderate applications. The pH and reference electrodes will be encased in a rugged, chemically-resistant Inconel body with a sealed, nonrefillable, long-lasting KCl gel diffusion reference electrode and a central measuring pH electrode. The electrode design was complete in FY 1981, but laboratory testing was not completed because funding to complete the work was not available at the time. Funding is now available and we anticipate that this electrode will be tested in the near future. Companion tests at PNL, and field testing, are scheduled during 1982 and 1983. If all goes well, the electrode should be commercially available shortly after the field testing program is completed.

Sulfide Ion Electrode

The third most important chemical component in geothermal fluids is dissolved hydrogen sulfide. This component plays a significant role in sulfide scaling, contributes to corrosion, and poses environmental hazards if released into surface waters or the atmosphere. In addition, sulfide content may need to be considered in making other measurements. Staff at Beckman Instruments of Anaheim, California, designed and completed preliminary laboratory testing of sulfide ion sensing electrode to partially fill this need.[21] Unfortunately, sulfide ion concentration in geothermal fluids is low; because of the pH found in these fluids. At the pH usually present, sulfur equilibria does not favor sulfide ion formation. If the design had been successful, the electrode may have partially met the required need. The design used a compressed silver, mixed with silver sulfide powder, for the sensor element; similar elements have been used to measure sulfide concentration in the laboratory and in other low-temperature environments. There has been little or no application or design experience with hydrogen sulfide ion sensors at the high temperatures and pressures of geothermal wells.

Preliminary tests showed that the electrode is workable to 220°C. Additional tests were needed to define the operating range of the electrode and its range of response to sulfide ion concentration; however, efforts to further develop this device were discontinued because of the low sulfide ion concentrations found in geothermal fluids, and advanced CSSD sensors may be more sensitive to the sulfur concentrations in geothermal fluids.

Chemically Sensitive Semiconductor Devices

Chemically sensitive semiconductor devices (CSSDS) offer a new and considerably more rugged class of devices for measuring the chemical properties of geothermal fluids. These devices

will be small, possibly no larger than the ordinary chip used in hand calculators, could be incorporated into a variety of configurations for both above-surface and downhole measurements and may be more versatile, measure several components simultaneously to provide more data, and be less costly than common sensors used today. The additional data should help to identify the more subtle nuances of solution chemistry affecting materials performance. CSSD's can also be designed to operate in the digital mode for simple data transmission. While they have obvious advantages, considerable research and development must be undertaken before they can be used widely for field measurements of pH, CO_2, calcium, sulfide as H_2S or S and other chemical species.

Work is underway at the University of Pennsylvania to develop these unique devices for geothermal use and other purposes. This work was funded by PNL during FY 1980 and 1981, but is now funded by DOE's Basic Sciences Division. The device operates in a fashion similar to a variable capacitor. A chemical component causes the ion selective layer to shift the capacitance of the diode structure. This shift can be measured and is repeatable for the ion being measured. An AC signal is impressed on the N-P junction for this measurement and the shift in capacitive reactance is measured. CSSD's also require a reference electrode. Other electronics include a power supply, phase change detector, and other minor components. A multipurpose CSSD could be constructed in a fashion similar to that used in fabricating calculator chips. Because of the large effort required to complete the research and development, we would not expect these devices to enter the market during the 1983-84 time period. When available, they could provide an accurate, reliable, and convenient means of measuring several ionic species in situ in geothermal brines and other systems.

FIELD TESTING

All devices successfully tested in the laboratory are expected to be field tested above ground in plant systems, or below ground in wells, as described below.

In-Plant Tests

The chemical sensors will be evaluated at the Magma Corporation 10 MW geothermal power plant, located at East Mesa, California, and successful devices will be installed at the power plant being designed by DOE, in cooperation with San Diego Gas and Electric Company, for demonstration at Heber, California. Pipe taps and bypasses, etc., have been incorporated into the piping and other equipment at appropriate locations for inserting the devices into the brine at the Magma Plant, and are being planned for the Heber operation. In concurrent programs, corrosion studies have and will follow the effect of the brine from the beginning of operation for at least two years. In addition, an intensive materials evaluation program is underway to ascertain the suitability of a variety of metals and other materials for geothermal use.

SUMMARY

DOE and PNL have a methodology and plan for providing new, advanced electrochemical sensors for geothermal use. Some of these prototype sensors completed laboratory testing; some are, or will soon be, field tested. In additon, new sensor concepts have been evaluated, research is underway to provide the data necessary for their manufacture, and we anticipate that the technology will be transferred to the user by 1984.

The high temperature sensors will provide the corrosion engineer and plant operator with a new set of tools identifying, evaluating, and reducing the adverse effects of harsh process environments. Though these devices are being developed for geothermal systems, they have applications in other process equipment as well, such as petroleum production refining, nuclear reactor power plants, chemical processing, pulp and paper production, and many others. In particular, the chemically sensitive semiconductor devices offer a means of monitoring a wide range of chemical species and identifying synergistic ionic effects which accelerate corrosion, or otherwise alter the performance characteristics of materials and processes.

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