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Synopses of R & D in Geothermal - Geochemical Engineering at the Lawrence Livermore National Laboratory
1976 - 1980

Compiled by
J. E. Harrar

MASTER

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DISCLAIMER

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Introduction

This report is a compilation of brief summaries of the R & D activities in Geochemical Engineering carried out by LLNL during the years 1976-1980 at the Salton Sea Geothermal Field, Imperial County, California. The accompanying references constitute a bibliography of reports in this area. Not included are accounts of our studies in materials and corrosion, reservoir engineering, and mechanical engineering, some of which have been reviewed elsewhere.

Previous reports that summarize LLNL geothermal work which may be of interest to the reader are a progress report of all LLNL work to January 1977,(1) a summary report of research on the total flow turbine concept,(2) a more detailed synopsis of the results of our studies in scaling and brine chemistry,(3) an interim review,(4) and LLNL industrial support program test results in FY 1979.(5)

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LLNL Geothermal Field Test Apparatus

In 1976 a field test facility was established by the Lawrence Livermore National Laboratory (LLNL) at the Salton Sea Geothermal Field for the evaluation of brine chemistry and materials problems such as corrosion and scaling.(1,2) The brine handling system was operated at various times until December 1979, with brine from one of two geothermal wells: Magmamax No. 1 and Woolsey No. 1. We coordinated our studies and the fluid handling with the well owners and operators, the Imperial Magma Company, and with the San Diego Gas and Electric Company in the operation of their Geothermal Loop Experimental Facility (GLEF).

The LLNL apparatus was configured initially as shown in Figure 1 to examine the corrosion/erosion characteristics of simulated turbine components (nozzles and wear blades), and to investigate the control of scale by brine acidification. This system enabled testing components and brine characteristics under three different conditions simultaneously.(1) We operated the well-head or first-stage separator (a centrifugal type) in all the experiments at a temperature of $\sim 210^{\circ}$C, ~ 250 psia, and an input flow rate of ~ 50 gpm at a steam quality of $\sim 10\%$. Spent brine was pumped into the GLEF injection line for disposal.

The system was then converted to a four-stage flash system, as shown in Figure 2, to obtain more detailed information on the corrosion of candidate plant materials and scaling rates as a function of temperature and brine pH. Finally, to carry out an investigation of the use of organic additives as scale control agents, the brine handling system was again modified, as shown in Figure 3, to a two-channel system. In the two-channel system there was one flash stage followed by a delay stage that simulated conditions in an atmospheric flash stage and reinjection line. To measure the effect of brine additives on scaling and corrosion rates, this system incorporated specimens of mild steel, Hastelloy, and Teflon, and Petrolite electrochemical corrosion monitoring equipment.

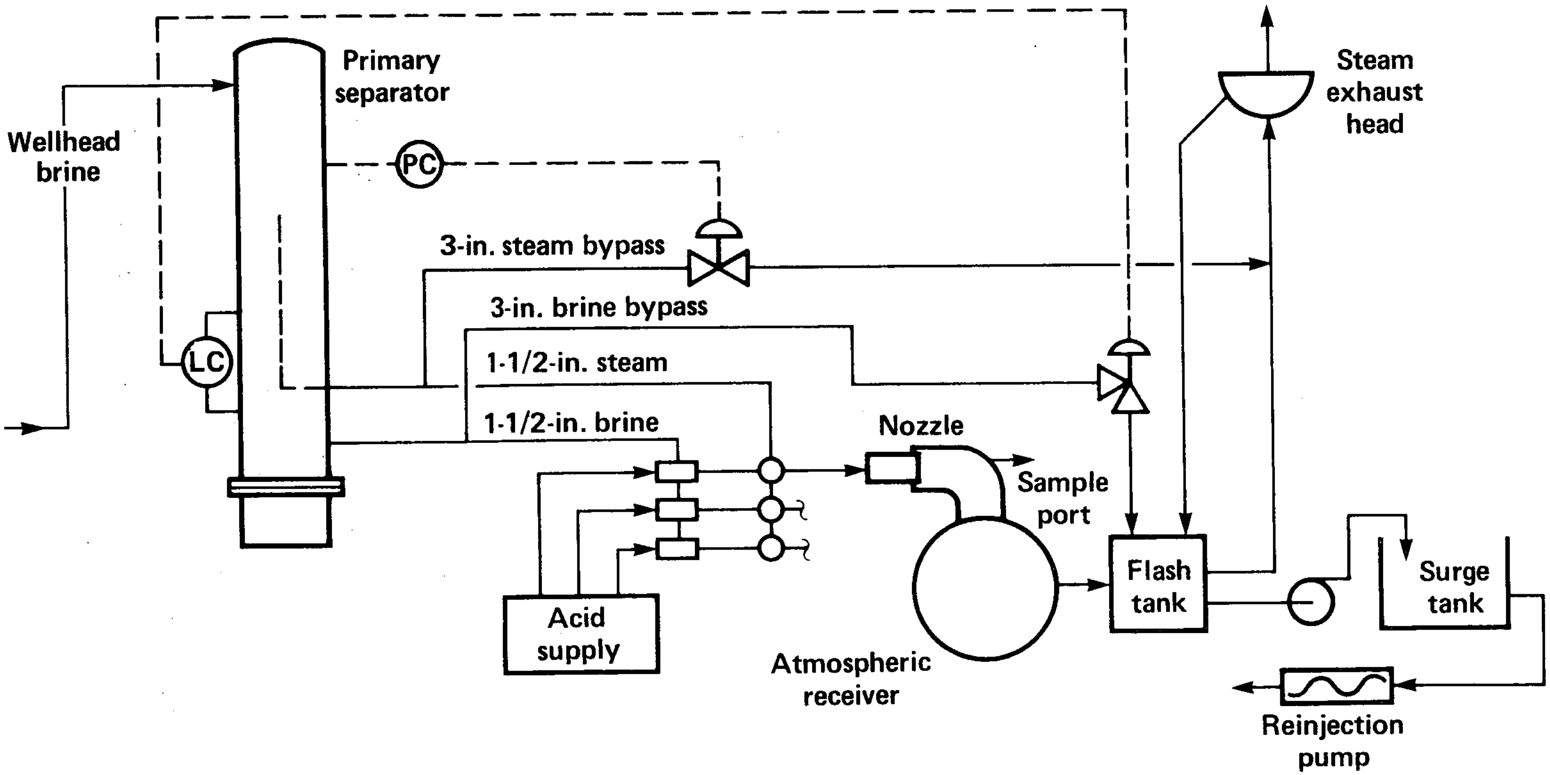

Figure 1. Simplified diagram of LLNL geothermal test system for studies of turbine components.

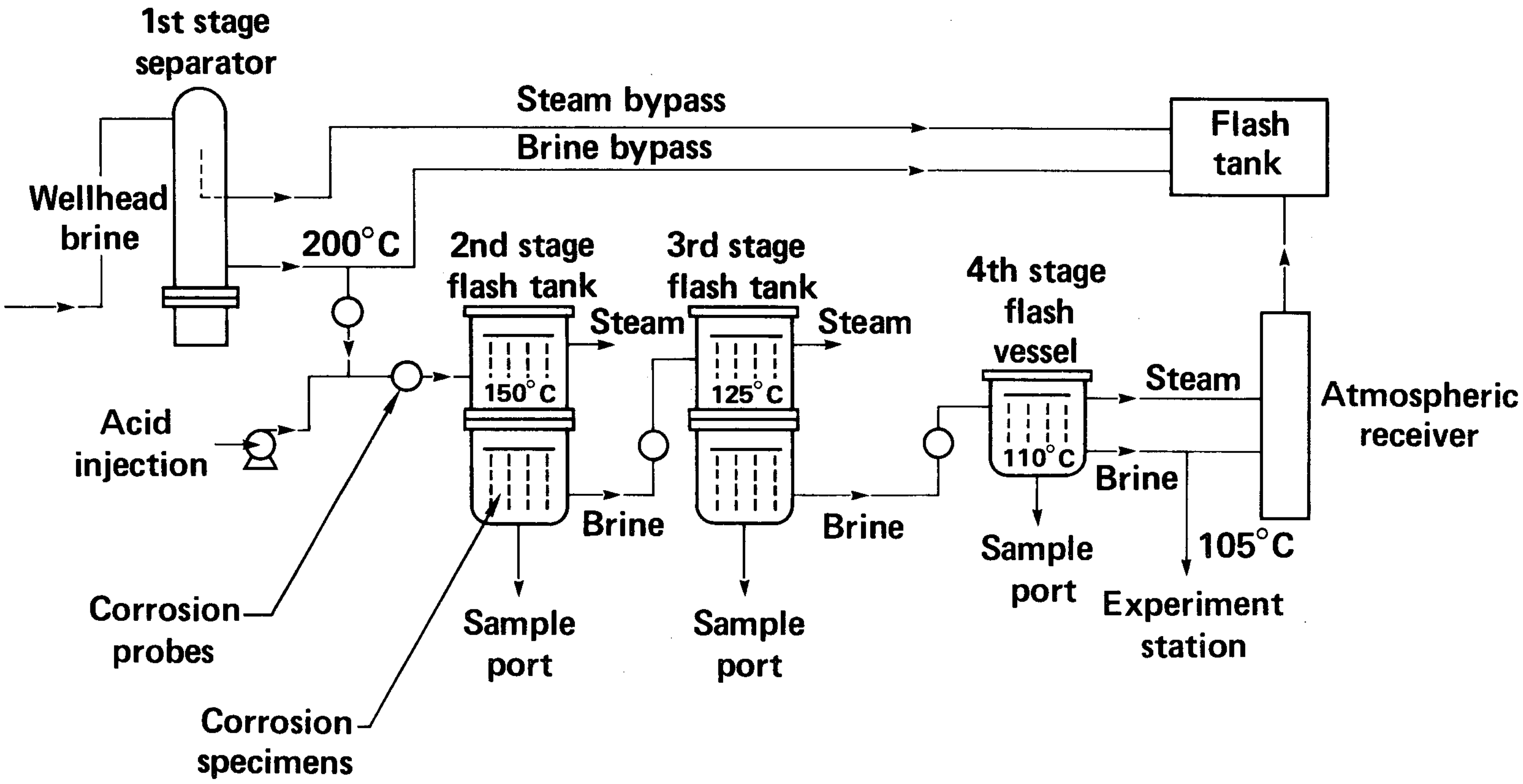

Figure 2. Simplified diagram of LLNL geothermal four-stage flash system.

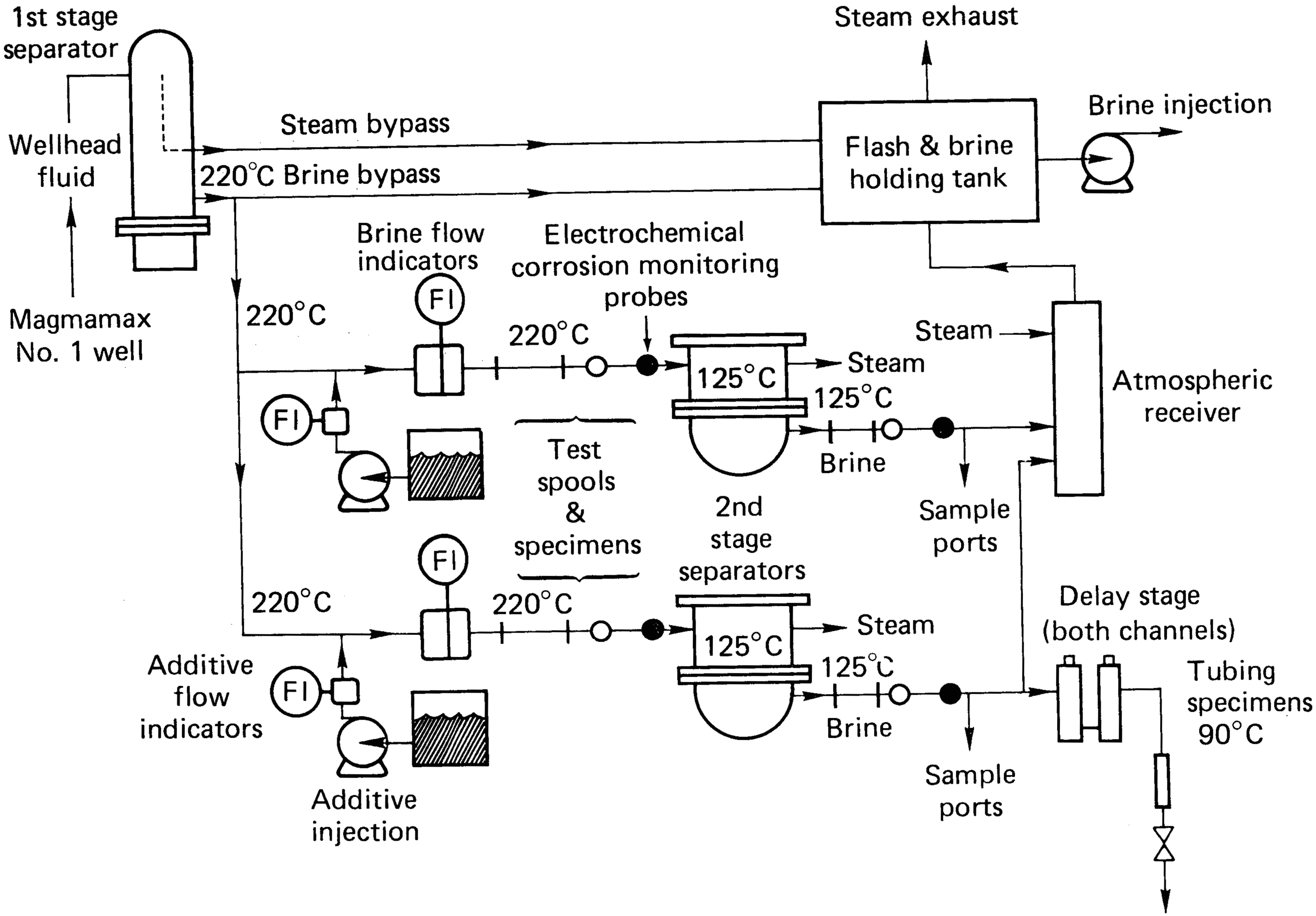

Figure 3. Simplified diagram of LLNL geothermal test system for studies of

The results of experiments in scale control and brine injectivity using these production-well systems are outlined below. The brine solids removal studies, pilot scale effluent treatment tests, and some of the injectivity testing were performed with another test facility constructed at the Magmamax No. 3 injection well.

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Brine Acidification as a Means of Scale Control at the Salton Sea Geothermal Field

Field experiments first carried out during 1976(1) showed that both sulfide and siliceous scale could be significantly reduced by lowering the pH of the brine by injection of hydrochloric acid. Brine acidification is the only chemical method discovered thus far that reduces the rate of growth of the high temperature sulfide scales. In subsequent field experiments, more detailed knowledge was obtained on the effect of brine pH on the rates of silica precipitation,(2) the nature of the solids precipitated,(3) the interactions of the processes of corrosion and scaling,(4) and the degree of scale reduction(3,5).

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Tests of Seeding and Other Chemical Methods for the Control of Scale at the Salton Sea Geothermal Field

Because the addition of previously precipitated silica in the form of a sludge had been shown to be effective in removing silica from geothermal brine,(1) this approach was also tested as a method of scale control.(2,3) Only a few experiments were performed because of equipment limitations, but it was clearly shown that the sludge seeding process reduced the level of silica supersaturation and retarded scale formation in straight runs of pipe.(2,3) It was concluded that this method of scale control had promise if brine handling equipment could be used that would tolerate the high levels of suspended solids.

Somewhat similar experiments in accelerating the rate of silica precipitation were carried out in which hydrogen peroxide or sodium hydroxide were injected into the brine. Both had the expected effect on the dissolved silica, but possible beneficial effects on the silica scaling rate were not assessed.(4)

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Tests of Proprietary Organic Additives for the Control of Scale at the Salton Sea Geothermal Field

In 1978 an industry solicitation was conducted for scale control agents that might be active toward the Salton Sea Geothermal Field scales. Nine of these were evaluated in field scaling tests and an additional eight formulations were evaluated as silica precipitation inhibitors.(1,2) Baseline scaling rates were found to be a strong function of brine salinity (TDS), which increased with production-well flow rate. The highest scaling rates, at the maximum well flow rates, were ∿0.1 mil/h (primarily sulfide scale) at 210°C, ∿0.8 mil/h at 125°C, and ∿5 mil/h at 90°C.

None of the proprietary additives were clearly effective in reducing the rates of scale formation, and none retarded the precipitation of silica. Although chemical additives for the control of calcite, gypsum, and other crystalline scales were well known, it appeared that there was no knowledge in the water treatment industry of how to retard the formation of metal sulfide and silica scales from geothermal brine.

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Tests of Generic Organic Compounds for Control of Scale at the Salton Sea Geothermal Field

In 1978 and 1979 a series of field tests was performed on approximately 120 different organic compounds of various types to determine their activity toward silica in the hypersaline geothermal brine. The compounds were first screened by determining their ability to inhibit the precipitation of silica. The most promising compounds were then subjected to scaling tests, during which corrosion measurements were also performed. In the course of the testing, certain functional groups emerged as most active, and ultimately 3 or 4 specific commercially available compounds appeared to be the most promising as antiscalants. The best degree of scale reduction that was achieved with a single additive (Corcat P-18) was a factor of 18 at 90°C. Although not thoroughly evaluated because of limitations on available testing time, it was concluded that the best additive formulation would probably be a mixture of compounds: an organic silica-precipitation inhibitor, a small amount of hydrochloric acid, and a phosphonate crystalline deposit inhibitor. Further knowledge was also developed on the mechanism of formation of scale from hypersaline brine and the action of the additives in retarding the silica scale.

The work was described in a series of transactions papers,(1-3) UCID reports,(4-7) a manuscript for journal publication,(8) a semi-technical account,(9) and some suggestions for future work.(10)

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Studies of the Dissolution of Geothermal Scale

To learn whether a practical method might be developed for the removal of the Niland scales from plant equipment by chemical means, laboratory experiments were performed in which well-characterized samples of scale from the GLEF were exposed to several low-cost mixtures of reagents.(1) The samples of scale were obtained from points throughout both trains of the GLEF after ∿1000-hr operations with Magmamax No. 1 and Woolsey No. 1 wells. The following treatments were tested for periods on 1, 4, and 24 hr. at 25 and 80°C : H_2O, 0.5 M NaOH, 0.5 M NaOH + 0.05 M EDTA, 0.5 M HCl, 0.5 M HCl + 0.13 M H_2O_2, 0.5 M HCl + 0.2 M HNO_3, 0.5 M HAC (acetic acid) + 0.5 M HNO_3, 0.1 M HF, and 0.1 M HF + 0.5 M HNO_3.

The predominantly silica scales were partially dissolved by hot NaOH and NaOH + EDTA, while the best reagent for dissolving the PbS-rich, high-temperature scale was HNO_3 with HF or HAC at 80°C. More concentrated solutions, particularly of compounds such as HF, would be much more effective, but would be hazardous to use. A combination of chemical and mechanical cleaning methods may be the most effective technique of scale removal.

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Chemical Measurement Developments

Several new techniques were developed for the measurement of the chemical parameters of the geothermal brines of the Salton Sea Geothermal Field. These include an insertable probe for acquisition of geothermal fluid samples,(1,2) an anaerobic incubation and analytical technique for following the rates of silica precipitation at 90°C,(3) and the application of laser particle counting techniques to the characterization of geothermal brines.(4) Related developments described elsewhere are techniques for brine injection testing and electrochemical corrosion rate measurement.

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Chemical Modeling of Geothermal Systems

Previously reported work(1) on the use of computer modeling to predict chemical equilibrium states of geothermal systems was extended and refined. The Helgeson-Herrick geochemical code was adapted and used to predict precipitation in brines at the Salton Sea Geothermal Field.(2,3) A predictive model was also developed for calculation of equilibria between liquid and volatile components of two-phase fluids.(4) A new chemical model based on the Newton-Raphson method of solution is described in detail with examples of model predictions for some geochemical systems.(5,6) A computer code for calculating the thermodynamic physical properties of geothermal brine/steam mixtures was also developed.(7) A detailed review(8) was presented of the available information on sulfide mineral precipitation and the chemical methods that might be used to avoid it in geothermal systems.

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Processing of Geothermal Brine Effluents for Injection

A process was developed for treating Salton Sea Geothermal Field brine effluents for injection.(1,2) Such effluents are chemically stable, low in suspended solids, and high in injectability. The process consists of solids contact clarification, in which the spent brine is first intimately contacted with sludge solids and then passed through a dense sludge blanket of silica-rich precipitated solids. The clarifier overflow stream is then polished by sand or precoat pressure filtration. Bench scale tests were conducted with inorganic and organic coagulants as a means of enhancing clarifier performance.(3) An anionic coagulant aid was found to be of significant benefit and was used in subsequent pilot clarifier tests. The pilot-sized reactor clarifier was tested at a flowrate of ∿10 gpm using brine effluents from the GLEF. Mixed-granular-media and diatomoceous earth pre-coat pressure filtration techniques were also tested. It was demonstrated that chemically stable brine effluents with 1-2 ppm levels of suspended solids can be produced. Injectability tests of these effluents (described below) indicated that these effluents can be disposed of by subsurface injection without significantly impairing injection wells at the Salton Sea Geothermal Field.

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Hydrogen Sulfide Abatement Using Geothermal Brine Effluents

A simple and potentially inexpensive method for removal of H_2S from noncondensible gases evolved in geothermal flash processes was successfully tested on a small scale in the field.(1) The method consists of scrubbing the noncondensible gases of H_2S with brine effluents which contain relatively high concentrations of Pb, Fe, and Zn such as those of the Salton Sea and Brawley Geothermal Fields. For plant applications, noncondensibles including H_2S would be ejected from a surface steam condenser (necessary to minimize the volume of liquid in contact with H_2S) and scrubbed with effluent brine just prior to preinjection clarification. The precipitated metal sulfides could be removed in the clarification process and the noncondensibles, without the H_2S, would be vented as usual.

Reference

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Study of Use of Surface Waters to Supplement Injection at the Salton Sea Geothermal Field

Three sources of local water (Salton Sea, New River, and Alamo River) were evaluated for use as makeup waters during injection. It was found that direct injection of makeup water was not feasible because of their high suspended solids levels and because mixing of the injection waters with geothermal brine effluent results in additional precipitation. However, mixtures of ambient temperature makeup water and higher temperature (80-90^{0}C) brine effluent, in a 1:4 mass ratio, are potentially injectable following processing by reaction clarification and granular media filtration.

Reference

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Measurement of Injectability of Geothermal Brines

Because the ability to inject "spent" geothermal brine is a critical and perhaps limiting factor in the development of the Imperial Valley resources, considerable R & D effort was directed toward an assessment of the injectability of the brines under various conditions. The approach was to measure the flow of brine through media that simulated or represented downhole injection formations, and then correlate these measurements, insofar as possible, with actual injection well performance. Because of the instability of the brine of the Salton Sea Geothermal Field with respect to the precipitaton of the iron-rich silica, all experiments were carried out in the field, on-line, and at effluent brine temperatures of 70-102°C.

The first studies were investigations of the characteristics of both untreated and acidified brine in core flooding(1) and membrane filtration(2) tests. It was shown that untreated effluent brines had very high suspended solids levels and that the injection of these brines would not be feasible unless the 1-μm and larger particulates were removed. Brines whose pH had been lowered to retard scale formation had markedly lower suspended solids levels, but this brine, at pH $\sim$4.5, is still not highly injectable without prefiltration.(3) Both manually operated(4) and automated(5) apparatus were used for the core flooding and membrane filtration experiments. These evaluation techniques were also applied to effluent brine produced by the LLNL pilot clarifier/filtration system(6) and the Imperial Magma 10 MW-size system(7) to verify their performance. In related work, the viscosity of the geothermal brines was determined as a function of temperature and ionic strength.(8; see also Ref. 3)

Apart from the work in the Imperial Valley, these techniques were also utilized in an assessment of injection problems at the Strategic Petroleum Reserve sites,(9,10) and recently in evaluating brine injectability at the DOE geopressured well in Brazoria County, Texas.(11)

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