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TECHNICAL REPORT
For the U.S. Department of Energy

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GEOHERMAL RESEARCH AT THE PUNA FACILITY
I.D. No. DE-FG03-85SF15799
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RESERVOIR ANALYSIS

The analysis is continuing and being extended to account for the possible precipitation of chemical species with special attention to the deposition of silica and the evolution of various gaseous phases.

SILICA CONTROL AND RECOVERY

This report consists of a summary of the experiments that have been performed to date at the Puna Geothermal Research Facility on silica in the geothermal fluid from the HGP-A Well. Also presented are some results of investigations on commercial applications of the precipitated silica. Seven data plots derived from project research and a discussion of work planned for the future are included.

Several experiments have been run to date on the precipitation characteristics of silica under a variety of conditions and the chemistry of the recovered material. Analysis of the brines have shown that the silica concentration in the high temperature brine (unflashed brine) has remained approximately constant at approximately 800 to 900 milligrams per kilogram in the brine since the well began production; after the brine is allowed to flash to atmospheric pressure and 100C (flashed brine), the concentration approaches 1100 mg/kg. These concentrations are five or more times the saturation limit in the liquid (depending on the temperature) but the silica remains as a meta-stable (polymerized -?- colloidal -?-) suspension that precipitates at a relatively slow rate with time. Analyses of molybdate-reactive silica in the unflashed brine show a slow approach toward a stable value of approximately 30% of the initial concentrations in the liquid phase over a period of 18 to 20 hours; approximately half of the reactive silica is lost in a period of less than two hours, however.

Analysis of silica precipitated in the percolation ponds and as pipe scale shows that the silica has a strong affinity for metal ions. Comparison of transition elements present in the silica and brine indicates that several elements are enriched in the solid phase well above their concentration in the liquid:

<u>ELEMENT</u>	<u>BRINE (ppm)</u>	<u>SILICA (ppm)</u>
Al	1.98	180
As	0.011	0.160
Cu	0.028	160
Fe	0.343	520
Pb	0.035	1.3
Se	0.003	0.033

Analyses of silica deposited in a heat exchanger (see figure) also show a very rapid deposition of metals along the length of the pipe in almost a chromatographic profile. An EPA leachability test (see attached table) indicates that the scavenged metals aren't highly labile although dilute acid washing can remove substantial amounts of the metals at moderate pH.

In order to test the precipitation characteristics of the silica, a series of tests were run to determine what factors control the rate at which silica is deposited in the brine. Initial tests indicated that deposition rates are relatively insensitive to temperature; rapid chilling of the brine does not accelerate the deposition appreciably whereas a modest change in pH, associated with flashing the brine to atmospheric pressure, brings about a very about a very rapid deposition of silica in the flash chamber. Quantitative tests of the precipitation rates showed that the recovery of silica from the brine (as indicated by the concentration of residual silica in the supernatant) is highly dependent upon the pH of the final liquid phase, and on the concentration of trivalent metal ion added to the brine. Although the silica versus pH plot shows a steep slope, when compared on the basis of ion concentrations, the more important variable appears to be the concentration of trivalent metal ion, at constant final pH, rather than hydrogen ion concentration. A very preliminary analysis indicates that iron salts are likely to be the most cost effective reagent for the removal of the silica from the brine.

An investigation of the possible use of the silica as a by-product for some industrial or agricultural application indicates that the silica can be used in a variety of processes but the most valuable application may be in specialty applications where its surface area could be of value. Surface area analyses of some of the early material recovered from natural precipitation from the brine ponds, and from the enhanced recovery

experiments indicated that the naturally precipitated material has a surface area of about 50 square meters per gram and that the artificially recovered silica has surface areas of up to 200 sq. M/g. The latter surface areas have not been achievable on a routine basis however and work is currently underway to determine what factors control precipitate surface area. Initial indications are that the final concentration of added metal reagent is not the governing factor but that the concentration at which the reagent is added may have some effect.

Experiments currently in the planning stages will investigate the addition of metal reagents to a hot pressurized brine upstream of a heat exchanger and determine what effects the following factors have on the recovery, precipitation rate, and particle size of the recovered silica: reagent strength, high-temperature residence time, final temperature, upstream versus downstream reagent addition, and low temperature residence time of the silica-reagent mix in the brine. We will also attempt to determine optimal operating characteristics for minimizing the fouling of the heat exchanger surfaces. Other tests that should be conducted are the possible effects of post recovery treatment on the silica surface area (e.g. pre-washing, acid leaching, and drying procedures (spray, tumble, batch)).

Other basic research questions that should be investigated involve the mechanisms of the silica precipitation process and the reasons for the ability of the transition metals to accelerate the rate at which silica solids form. One basic question that remains in doubt is what step controls the rate of the precipitation process; two possible candidates are the dehydration reaction of silicic acid to free silica and water or the bond formation step between silicic acid (or free silica) and an existing polymer chain. The pH effect on the rate of silica precipitation suggests that the former is important. However, silica polymers have been shown to have very strong surface charge that is highly dependent on solution pH and hence the surface charge effects may be limiting the rate of polymer chain growth. Laboratory experiments on the combined effects of transition metals concentration and pH and spectroscopic studies of the silica rich brine are currently being developed to try to better investigate these processes.

Bill Chen
Principal Investigator

SILICA CONCENTRATION IN HGP-A BRINE

SILICA VERSUS TIME

CONCENTRATIONS OF METAL IONS IN HEAT EXCHANGER SCALE

CONCENTRATIONS OF METAL IONS IN HEAT EXCHANGER SCALE

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Certification No. 154

RCRA HAZARD ASSESSMENT ANALYSIS REPORT

INALAB

UH GEOTHERMAL
2525 Correa Road
Honolulu, Hawaii 96822

REPORT DATE: 11/8/85
ANALYSTS: W. Chao, I Enoki
J. Terrill
INVOICE NO: 7012
P.O. NO: 4977-120

Attention: Dr. Don Thomas (telephone: 948-6482)

Sample Description: HGP-A Percolation Pond INALAB No.851017-33

The sample identified above has been analyzed for the following characteristics of a potentially hazardous waste:

IGNITABILITY [] CORROSIVITY [] REACTIVITY [] METALS [X]

Methodology and analysis selection are in strict accordance with regulations and guidelines specified in the Federal Register, 40 CFR Part 261.

*****RESULTS*****

Part 261.21 IGNITABILITY
FLASH POINT < > NA°F (Min. allowed 140°F) ORGANIC LAYER ONLY!

Part 261.22 CORROSIVITY
pH NA (2< pH <12.5 allowed) DEFINED FOR AQUEOUS SYSTEMS ONLY!

Part 261.23 REACTIVITY
Acid labile cyanide < > NA ppm (w/v)
Acid labile sulfide < > NA ppm (w/v)

Part 261.24 METALS: EP TOXICITY [X] TOTAL []

Sample Type: Aqueous 27% Organic____% Solid 73%

Element	Concentration mg/L Aqueous	Maximum Allowed, mg/L E.P CRITERIA ONLY!
Arsenic	0.022	5.0
Barium	<5.0*	100.0
Cadmium	<0.01*	1.0
Chromium, total	<0.05*	5.0
Lead	<0.1*	5.0
Mercury	<0.002*	0.2
Selenium	<0.001*	1.0
Silver	<0.01*	5.0

* = Detection limit.

NA = Not Analyzed.

Industrial hygiene surveys • SCUBA air analyses • Asbestos bulk and air sampling and analysis • Organic vapor and permanent gas analyses • Trace metal analyses • Mineral dust analyses • Method development and research
Mass Spectrometry • Expert Witness/Litigation • Hazardous waste evaluation

SILICA VERSUS pH

SILICA VERSUS FE_3+ (MG/KG)

pH=8

SILICA VERSUS AL₃+(MG/KG)

pH=8