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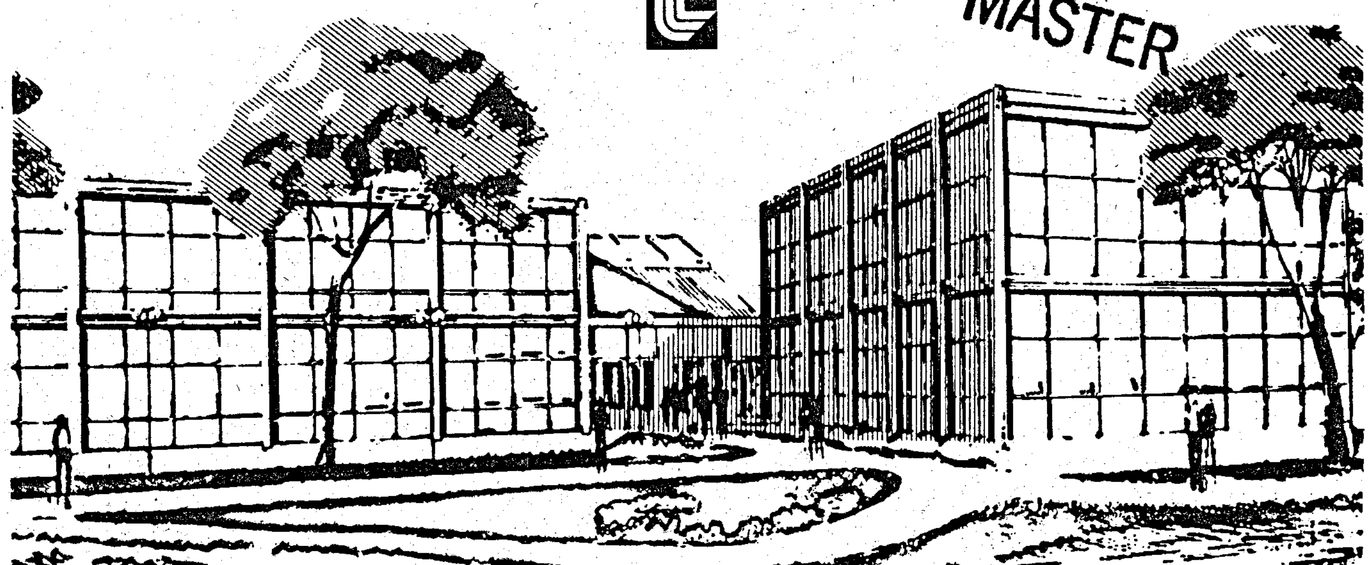

# Sampling and Characterization of Suspended Solids in Brine from Magmamax #1 Well

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## ABSTRACT

When high temperature, high salinity geothermal brines are cooled, appreciable quantities of solids precipitate. These suspended solids can cause extensive erosion and plugging in power plant components. In addition, there is considerable concern that reinjection of these solids with spent brine may plug the geologic formation adjacent to the reinjection wells. This report describes work done to sample these solids and characterize them so that processes can be devised for their removal or control.

Suspended solids produced in brine from Magmamax #1 well consist primarily of an iron-rich amorphous silica gel. A sampling apparatus to filter these solids out of high temperature, high pressure brine streams is described. Their chemical composition and physical description is discussed. Rates of production of suspended solids are given for brines flashed through nozzles and flashed in steam separators. Control of solids production by acidification to a pH <4.5 is described. At this time, control by acidification seems to offer an attractive alternative to conventional methods (filtering, settling, etc.) for removing suspended solids from spent brine prior to reinjection.



## INTRODUCTION

When high salinity brine from the Salton Sea Geothermal Field (SSGF) is cooled, sparingly soluble constituents precipitate. Most of these solids remain in suspension as brine flows through energy conversion equipment. Unfortunately, process equipment handling high velocity brine and solids can be rapidly and severely damaged by erosion. Also, these solids plug valves and piping and may shorten the lifetime of reinjection wells by destroying geologic formation porosity. This report describes work done to sample these suspended solids and characterize them both physically and chemically so that problem areas can be identified and control techniques can be evaluated. This work was done with brine from Magmamax #1 well which is located in the Salton Sea Geothermal Area and operated by Magmamax Power Co. Some of the samples were taken from the San Diego Gas and Electric Co. Geothermal Loop Experimental Facility (GLEF).

Others were obtained from the Lawrence Livermore Laboratory Field Test Unit (LLLFTU).

## RESULTS AND DISCUSSION

The apparatus used to collect suspended solids from high temperature, high pressure brine lines is shown in Figure 1. Originally, three sintered stainless steel filters were used in this apparatus to obtain a particle size distribution for the solids. The pore size of the filters was 165, 65, and 10 μm. After examination of the collected solids indicated that they were composed primarily of an amorphous iron-rich silica gel, only the 10 μm filter was used. In use, the apparatus is fitted with valves and a pressure gauge so that the differential pressure across the filter can be regulated to $<10$ psi. Samples were taken from 10-in. brine lines by attaching this apparatus to a traversing sample probe (1). This probe is designed so that it can be inserted through a valve and traversed from one side of the pipe to the other. Thus it is possible to obtain a sample of the brine that is relatively free of solids that have collected on the wall of the pipe or around the valve. To avoid errors caused by the precipitation of solids when brine contacts the cold probe, the probe is heated by running the hot brine through a bypass before the valves on the sampler are opened.

Chemical analyses of samples of suspended solids taken from the pipeline near the reinjection well of the GLEF are shown in Table I. These results indicate that the solids are rich in Fe and Si. Minor amounts of heavy metals such as Pb and Zn are also present. X-ray diffraction analysis indicates that the iron-rich silica matrix is amorphous. Also, the heavy metals occur primarily as sulfides. These samples also contain a considerable amount of Ca and Mn which occur primarily as carbonates. Their presence is attributed to the reinjection of high pH (9 to 10) condensate into the spent brine during this period of operation.

Suspended solids taken from the brine at Magmamax #1 wellhead and from the separator on the LLLFTU were found to be almost pure PbS. Electron micrographs of these solids are shown in Figure 2. These micrographs and chemical analyses indicate that these solids are submicron sized-crystals of PbS which are cemented into larger agglomerates.

Electron micrographs of suspended solids taken from the reinjection pipeline of the GLEF are shown in Figure 3. These micrographs show the typical silica gel structure of the amorphous iron-rich silica matrix. This is the same structure previously found in silica scale deposited from geothermal brines.

The extent of solids production in the GLEF and the LLLFTU was determined by sampling suspended solids at the Magmamax #1 wellhead, the separator of the LLLFTU, the reinjection pipeline of the GLEF, and from brine which had been expanded through nozzles to atmospheric pressure in the LLLFTU. These results are shown in Table II. These data indicate that brine from Magmamax #1 wellhead contains about 26 ppm of suspended solids. However, about 475 ppm of suspended solids are produced when brine is flashed to remove steam in the GLEF or when brine is flashed through nozzles to atmospheric pressure in the LLLFTU. For a 100-MW powerplant, 475 ppm of suspended solids corresponds to approximately 5 tons/day which would be reinjected with the spent brine.

The time elapsed before solids will plug a reinjection well depends largely on the porosity and fracturing that exists in the formation. However, there can be little doubt that plugging will eventually occur. Therefore, methods must be developed either to prevent the formation of solids in process brine or to remove solids from the spent brine. One technique that we have tried to inhibit the formation of solids is acidification.

The rate of suspended solids production in Magmamax #1 brine was determined as a function of pH during acidification experiments conducted in October and November, 1976. In these experiments, separated high temperature (220°C), high pressure (250 psi) brine was acidified and expanded through nozzles in the LLL brine modification apparatus to atmospheric pressure. Samples used to determine suspended solids production were taken from elbows in the exhaust system about 16 inches downstream from the nozzles. The temperature of the brine at the sampling point was about 95°C. All samples were transferred to a constant temperature bath at 85°C immediately after they were taken. To determine the rate of solids production, the samples were removed from the constant temperature bath at timed intervals and immediately filtered through glass frits with a nominal pore size 4 to 5.5 μm. The solids were then washed with distilled water, dried at 110°C and weighed.

Initial experiments were conducted over intervals up to 24 hrs. with samples in the pH range from 1.6 to 5.8. Results are shown in Figure 4. These data indicate that the precipitation of suspended solids from Magmamax #1 brine in this pH range is essentially complete in 4 hrs. or less. They also show that acidification of the brine to a pH $<4.5$ greatly inhibits the production of suspended solids. The amount of solids produced at a pH $<4.5$ is $<1/10$ the amount produced in unmodified brine (pH 5.8). These results were confirmed by additional experiments conducted over shorter time intervals.

The quantity of suspended solids produced as a function of pH in a 4 hr. time interval is shown graphically in Figure 5. This figure emphasizes the decrease in solids production as the brine is acidified to a pH $<4.5$. It shows that over 400 ppm of solids precipitated from unmodified brine (pH $>5.8$). However, acidification of the brine to a pH $<4.5$ reduced solids production to $<30$ ppm.

The solubility of precipitated solids in acid solutions was also investigated. In this experiment, a 5 gallon sample of brine was taken from Magmamax #1 well and allowed to cool to ambient temperature. Aliquots of the brine together with its suspended solids were then treated as shown in Table III. These data indicate that the unmodified brine contained 580 ppm of suspended solids. They also show that <1/3 of the solids redissolved when the brine was acidified to concentrations as high as 1.0 M HCl together with 0.1 M $HNO_3$. Therefore, it does not seem practical to remove solids from cold brine by redissolving them with acid.

Removal of suspended solids from spent brine by conventional techniques such as settling or filtration are additional alternatives. The primary disadvantage of these techniques stems from the tremendous amounts of brine that must be handled to remove relatively small amounts of solids. Also, some techniques may have adverse environmental impacts. For instance, leakage from settling ponds could destroy valuable farm land which surrounds the geothermal sites. In addition, there would be a problem associated with disposal of some solids even if most of them were processed for mineral recovery.

In conclusion, the solids produced when brine from Magmamax #1 well cools consist primarily of an amorphous iron-rich silica matrix with minor amounts of heavy metal sulfides. Acidification of Magmamax #1 brine to a pH <4.5 inhibits the formation of these suspended solids and seems to be a promising technique for the control of solids production. Because the solid forming constituents remain dissolved in solution, they do not cause erosion and plugging of conversion equipment. Also, they can be reinjected with the spent brine. Thus, problems associated with the removal of suspended solids from spent brine and with their disposal are avoided.

## ACKNOWLEDGEMENT

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## REFERENCES

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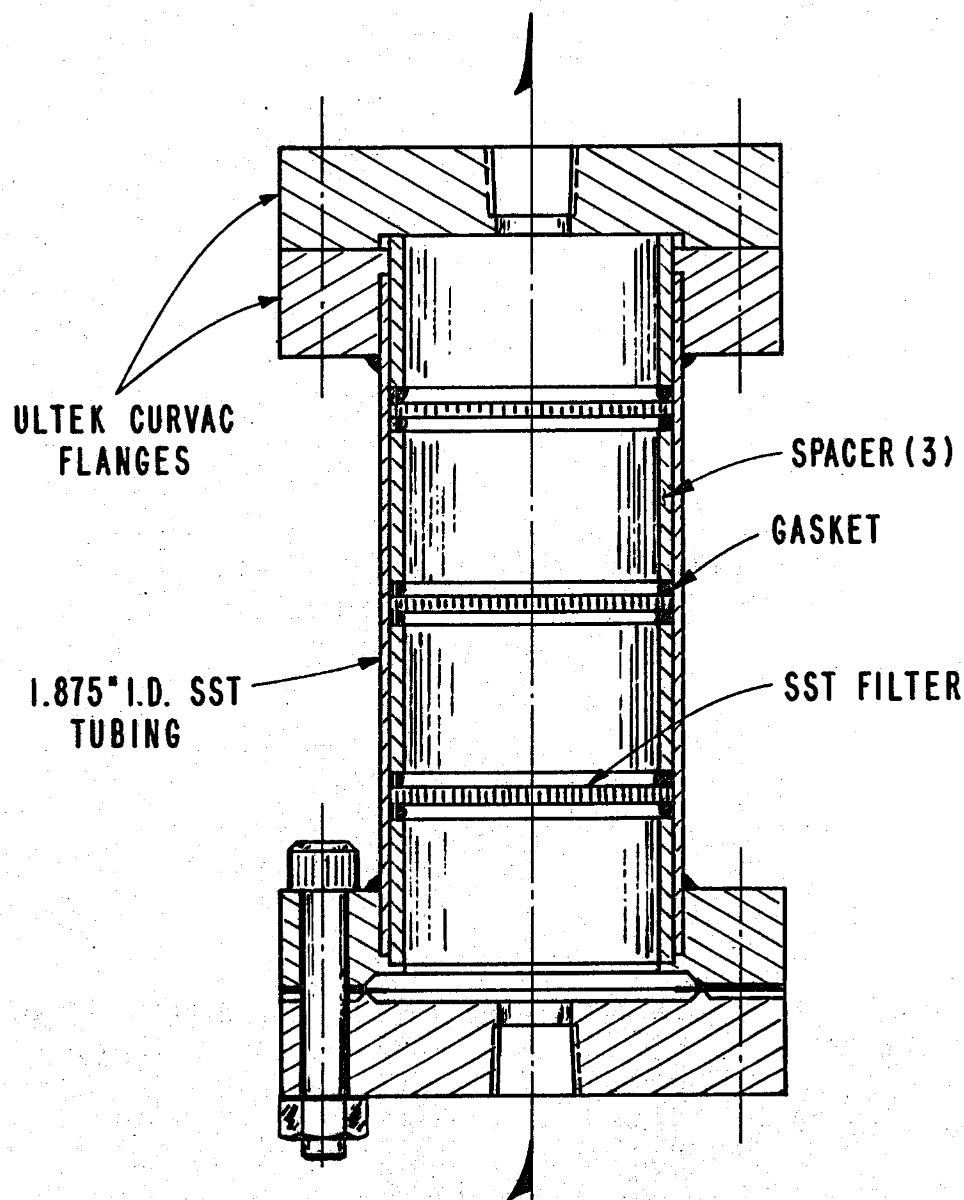


FIGURE I

SUSPENDED SOLIDS SAMPLER

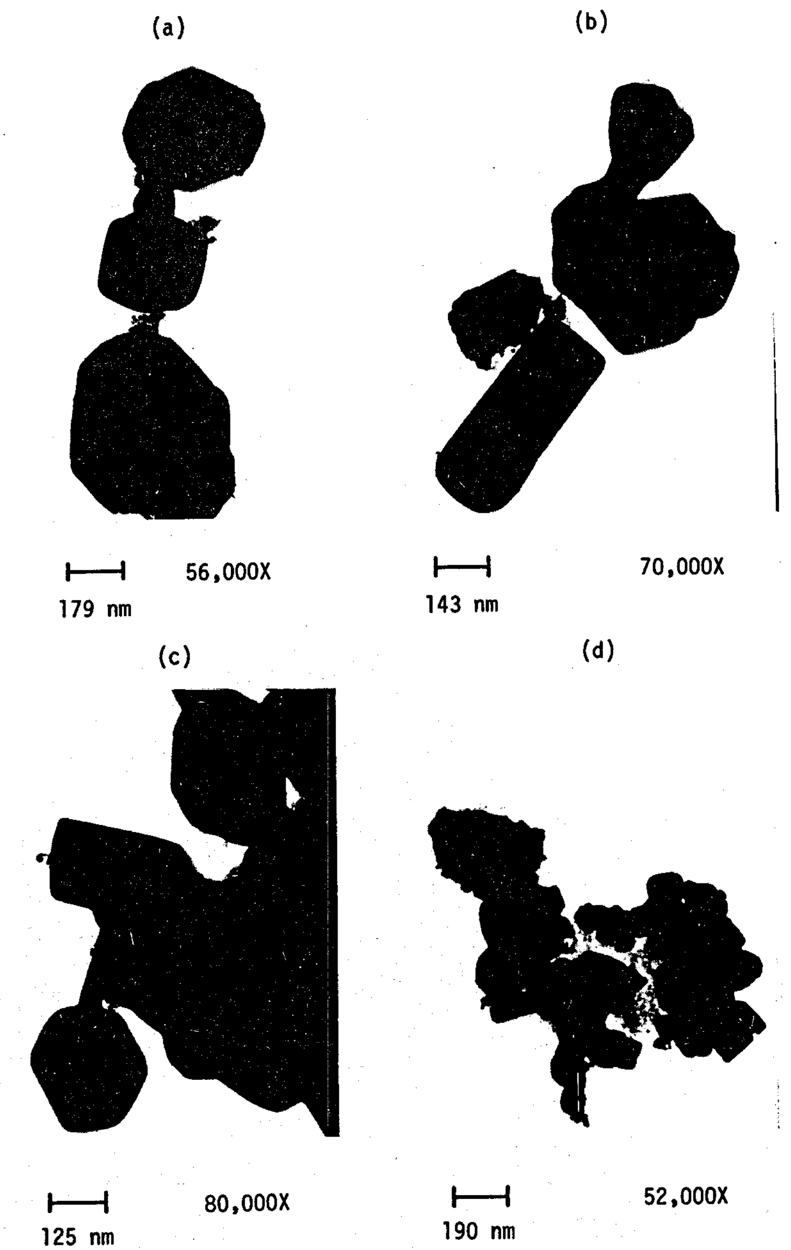


Figure 2

Electron Micrographs of Solids
from Magmamax #1 Wellhead

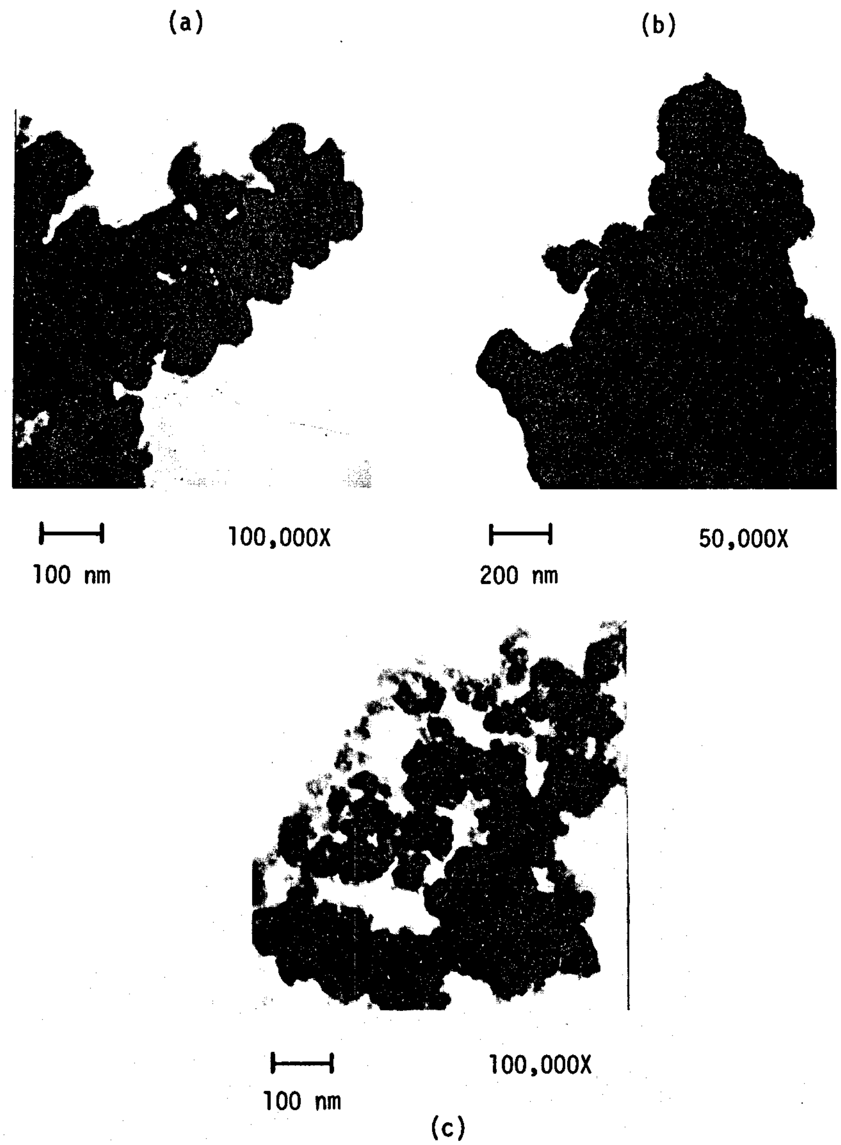


Figure 3

Electron Micrographs of Solids
from GLEF Reinjection Line

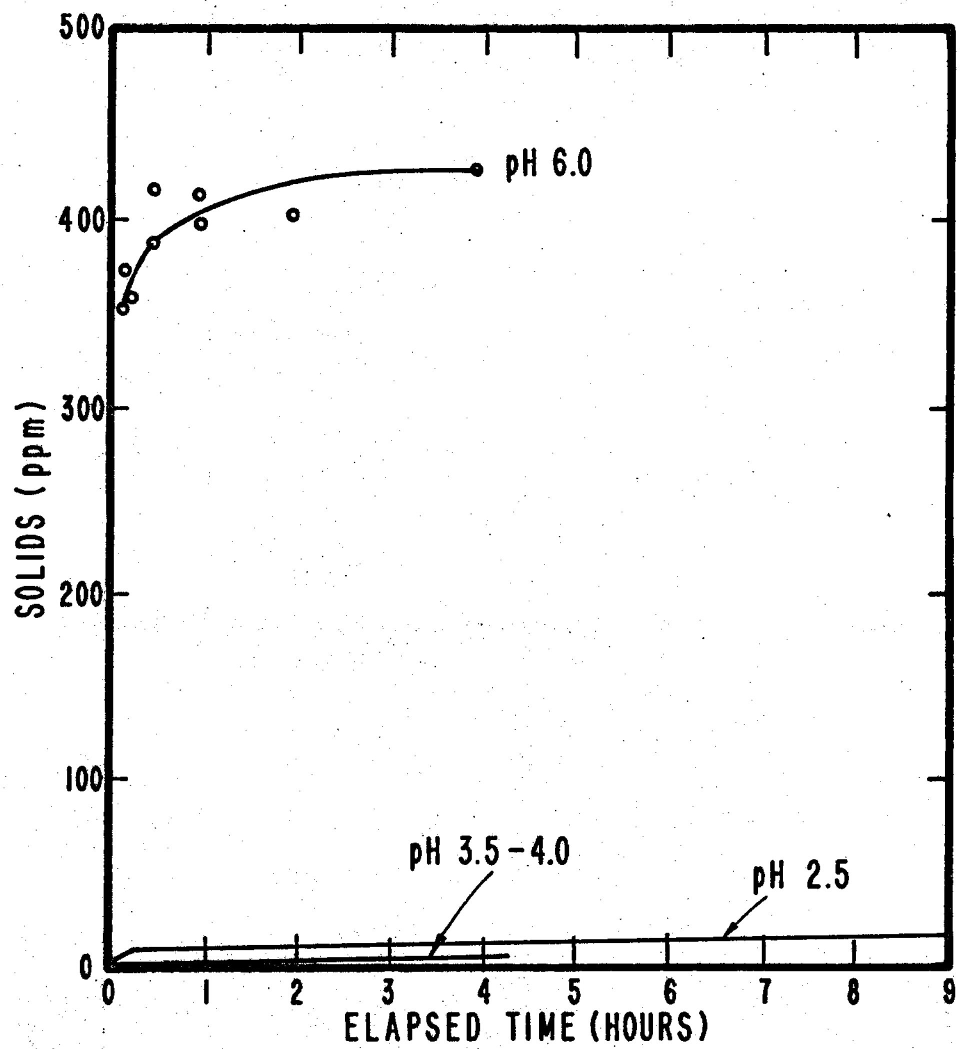


FIGURE 4

RATE OF SOLIDS PRODUCTION AT 85° C
IN SEPARATED MAGMAMAX No. 1 BRINE

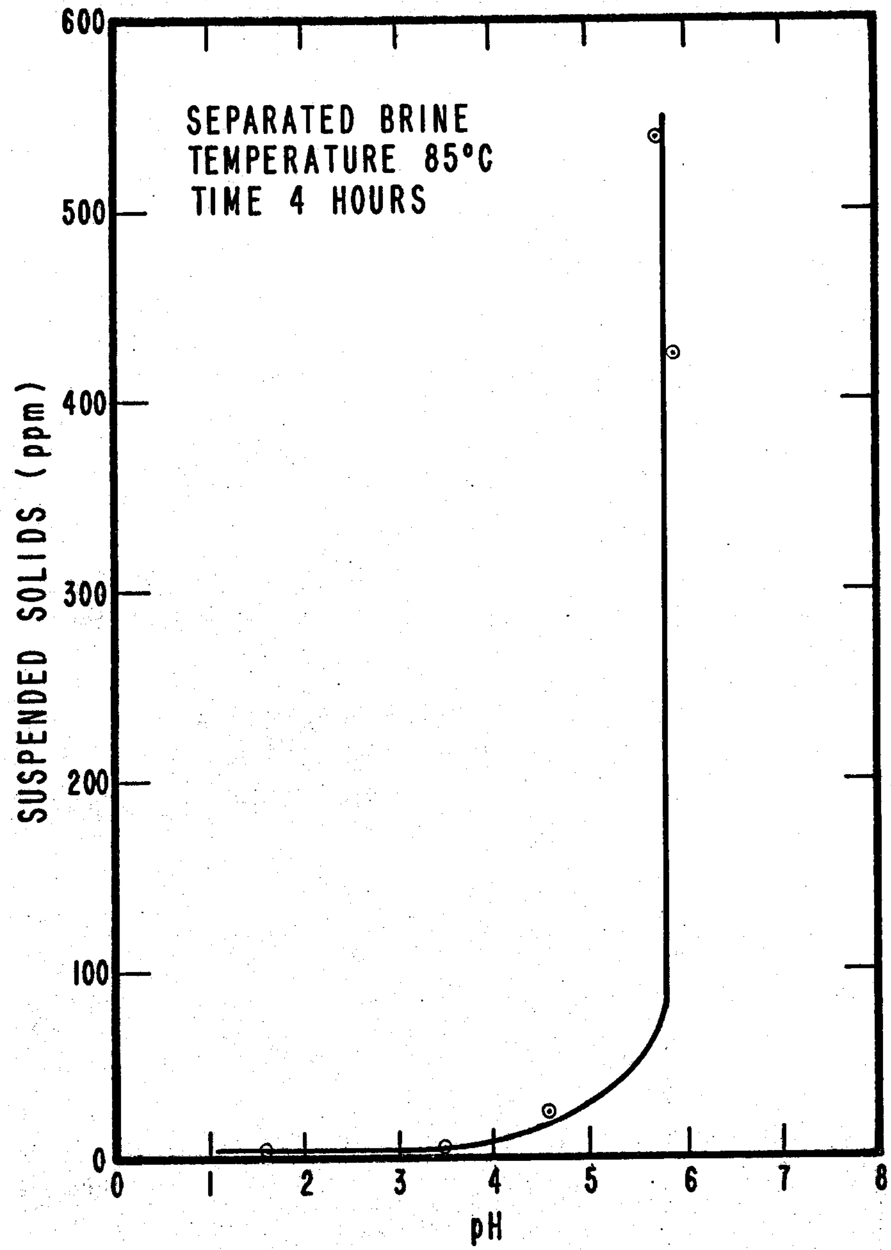


FIGURE 5

SUSPENDED SOLIDS PRODUCTION AS A FUNCTION OF pH

Table I. Semi-Quantitative Analysis of Suspended Solids from the GLEF

Temperature 90°  Pressure 150 to 300 psi

| ELEMENT | Wt. % (normalized to 100) MX-3-L12 FILTER SIZE 65 µm | MX-3-L12 10 µm | MX-3-L14 FILTER SIZE 65 µm | MX-3-L14 10 µm |
|---|---|---|---|---|
| Si | 50 | 43 | 32 | 30 |
| S | 1.7 | 0.9 | 0.7 | 0.4 |
| Ca | 10 | 5.4 | 4.4 | 1.9 |
| Mn | 3.0 | 4.6 | 4.1 | 3.0 |
| Fe | 28 | 37 | 48 | 57 |
| Cu | 0.5 | 0.6 | 0.8 | 0.3 |
| Zn | 1.6 | 2.1 | 1.2 | 0.8 |
| As | 0.3 | 0.6 | 0.5 | 0.8 |
| Sr | 0.03 | 0.09 | 0.03 | 0.05 |
| Mo | 0.01 | 0.009 | 0.03 | 0.04 |
| Ag | 0.009 | 0.06 | 0.003 | 0.003 |
| Cd | 0.003 | 0.006 | - | - |
| Sn | 0.01 | - | 0.003 | 0.004 |
| Sb | 0.003 | 0.15 | 0.03 | 0.04 |
| Ba | 0.13 | 0.6 | 0.08 | 0.14 |
| Pb | 1.4 | 4.5 | 1.0 | 1.1 |

Table II. Suspended Solids Production

| Brine Sample | Concentration of Solids mg solids/Kg brine | Composition of Solids |
|---|---|---|
| Magmamax #1 Wellhead | 26 | PbS |
| Separated Brine | 20 | PbS |
| Expanded through nozzle | 475 | Fe-Si matrix with minor PbS |
| Magmamax #3 Reinjection line from GLEF Operation | 480 | Fe-Si matrix with minor PbS and ZnS |

For a 10-MW powerplant using 800,000 lb/hr of brine, solids production would be approximately 5 tons/day.

Table III. Response of Suspended Solids to Acid Treatment

| Treatment | Concentration of solids after treatment[a] mg/Kg brine |
|---|---|
| None | 580 |
| Acidified to pH 4.1, allowed to stand 5 hrs. at room temperature. | 615 |
| Acidified to pH 2.0, allowed to stand 5 hrs. at room temperature. | 460 |
| Acidified to pH 2.0, allowed to stand 3 hrs. at 90°C. | 400 |
| Leached 1 hr. in 1 M HCl, 0.1 M $HNO_3$ at 50°C. | 390 |

[a]All samples were filtered, washed with $H_2O$ and dried at 110°C.