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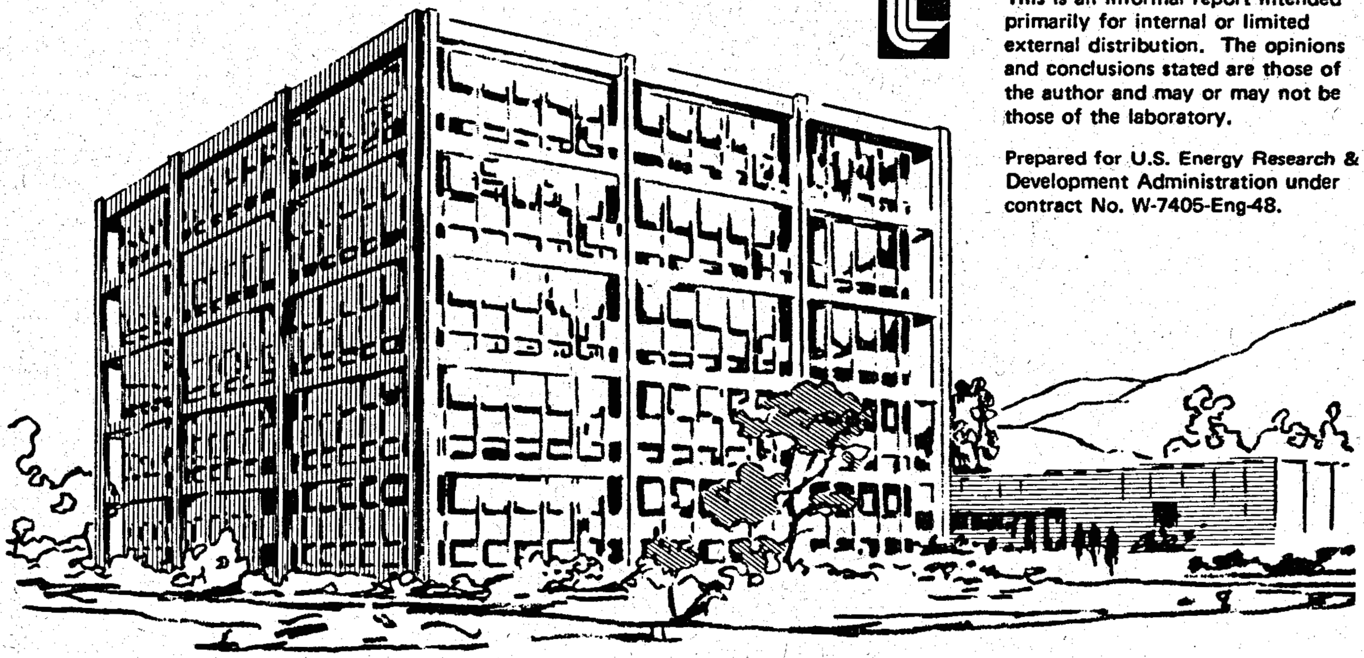

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Introduction

This report is a preliminary description of the results obtained in the analysis of the effluent brine from the LLL four-stage flash system. Of principal interest was the rate of formation of suspended solids and the rate of decrease of dissolved silicon (or silica) in the solution as a function of the pH of the effluent brine. The experiments were conducted using Magmamax No. 1 brine at the LLL Test Facility near Calipatria, California. The well-head brine (having a pH of ∿5.7) was acidified in the flash system to pH values of 5.0, 4.0, and 3.0, ±0.2 pH unit, and the solids and silica in the effluent at ∿90°C were measured, respectively, by filtration and atomic absorption spectrophotometry. Changes in solids and silica concentration were determined after holding the brine at 90 ± 5°C for periods of time up to one week.

Experimental

The quantity of suspended solids in the brine was determined by filtration of 100 to 200 ml of brine through Corning No. 32960, 30-ml, fine-porosity crucibles. The maximum pore size of these crucibles is specified as 4.5 to 5.0 μm; a particle size greater than ∿5 μm diameter is therefore defined here as constituting suspended solid material. The concentration of silicon in the filtrate was determined by immediate acidification and measurement by standard addition using the techniques of atomic absorption spectrophotometry. Both truly-dissolved silica (monomeric of polymeric), and solid particles less than ∿5 μm diameter are determined, and are reported, as dissolved silica for the purposes of these experiments. After collection of the suspended material on the filter crucibles, the crucibles are rinsed with water, dried at 105°C in an oven, cooled in a desiccator, and weighed.

Samples of brine held in incubation at 90 ± 5°C for periods up to 8 hr were contained in 4-oz screw-cap glass bottles filled to the top. Samples held for periods of 8 hr and longer were sealed under nitrogen in special glass ampoules to prevent reaction of air oxygen with the Fe(II) in the brine. These ampoules, 5-cm diam x 15-cm high, were opened when required by means of a hot-wire technique. All operations involving brine sampling and containment were carried out as rapidly as possible to prevent cooling below 85°C and/or reaction with oxygen. Previous work at this laboratory has shown that the nature of the solids formed from brine is markedly different in the presence of oxygen. The brine incubation containers have straight sides, and an attempt was made to remove all of the precipitates from the inside walls using a rubber policeman. When difficulty in filtering was encountered, a sample of the filtrate was taken immediately for silica analysis.

Results and Discussion

The experiments on solids formation were performed on brine effluent from the fourth stage of the flash system. The gross composition of this brine, as it varied during these tests, is summarized in Table 1. There was a significant change on September 22 because of the additional well flow, but this increase in the strength of the brine probably does not affect the precipitation of the silica appreciably.

Table 1. Analysis of brine from 4th stage
(Sampled at 105°C, before the delay line)

Date	Density	Total Solids %	Chloride N	Chloride %	SiO_2 ppm
9/15					445
9/17	1.141	19.0	3.63	11.3	452
9/19	1.145	19.9	3.65	11.3	452
9/21	1.143	19.4	3.70	11.5	458
9/22[a]	1.172	22.5	4.47	13.5	477

[a] San Diego Gas & Electric Co. also drawing brine.

At the fourth-stage, the brine is flashed to atmospheric pressure at a temperature of ∿105°C. At the brine output from the fourth stage, the system is provided with a "delay line" or length of pipe, from which an effluent could be obtained that had, in effect, been held at near flashing temperature for an additional 20 min. The additional transit time and the additional temperature drop to 88-90°C were expected to generate additional suspended solids in the effluent, and this was tested in an initial series of experiments. It was found that, at the input to the delay line (the 105°C output of the fourth stage), the suspended solids in unmodified brine averaged 41 ppm, and the silica in the filtered brine amounted to 411 ppm as SiO_2. After the 20-min delay line, the effluent contained 100 ppm solids and the filtrate 353 ppm SiO_2. Thus for unmodified brine the delay line had a significant effect. In subsequent studies brine for the measurement of changes in solids and silica was taken from the output of the delay line, but for comparison of the effects of incubation time and pH, the graphical data are referred to the time when the brine exited the fourth stage.

From pairs of duplicate measurements in the range of 50-500 ppm, the standard deviations of the measurements of SiO_2 and solids are 6 and 13 ppm respectively.

One experiment was conducted to determine the effect of acidification on freshly precipitated solids and silica in solution. Two 90°C samples of unmodified brine (pH 5.98) were obtained and incubated for 30 min. One sample was then acidified to pH 1.7, allowed to stand for 5 min; then both samples were filtered and SiO_2 in the filtrate was determined. The quantity of filtered solids dropped from 214 to 181 ppm upon acidification, but the SiO_2 concentration remained constant at 300 ppm. Thus little, if any, SiO_2 redissolved under these conditions.

The results obtained thus far in the study of the precipitation of solids and SiO_2 from the brine are shown in Figures 1 and 2. The results in general bear out previous investigations[1] showing the beneficial effects of acidification of the brine to prevent solid formation. Samples of the brine are still being incubated at 90°C to obtain further long-term stability data. It is apparent that above pH 4, significant solids formation cannot be postponed longer than 24 hr. All measurements presented in this report were obtained during acidification of the brine between the first and second flash stages. One plant run with acidification between the second and third stages, at a pH of 4, revealed no significant difference in the behavior of the solids and silica in the effluent.

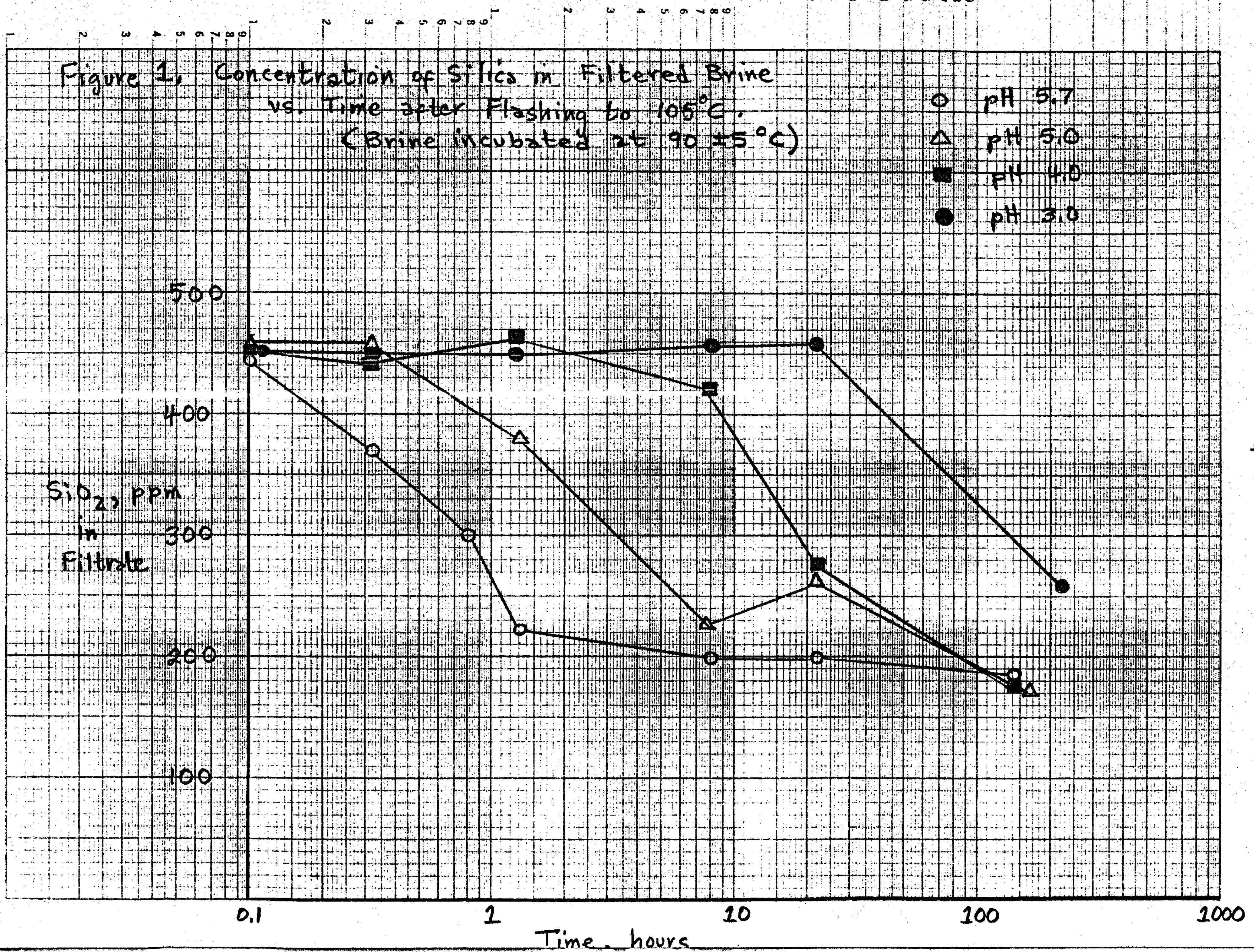
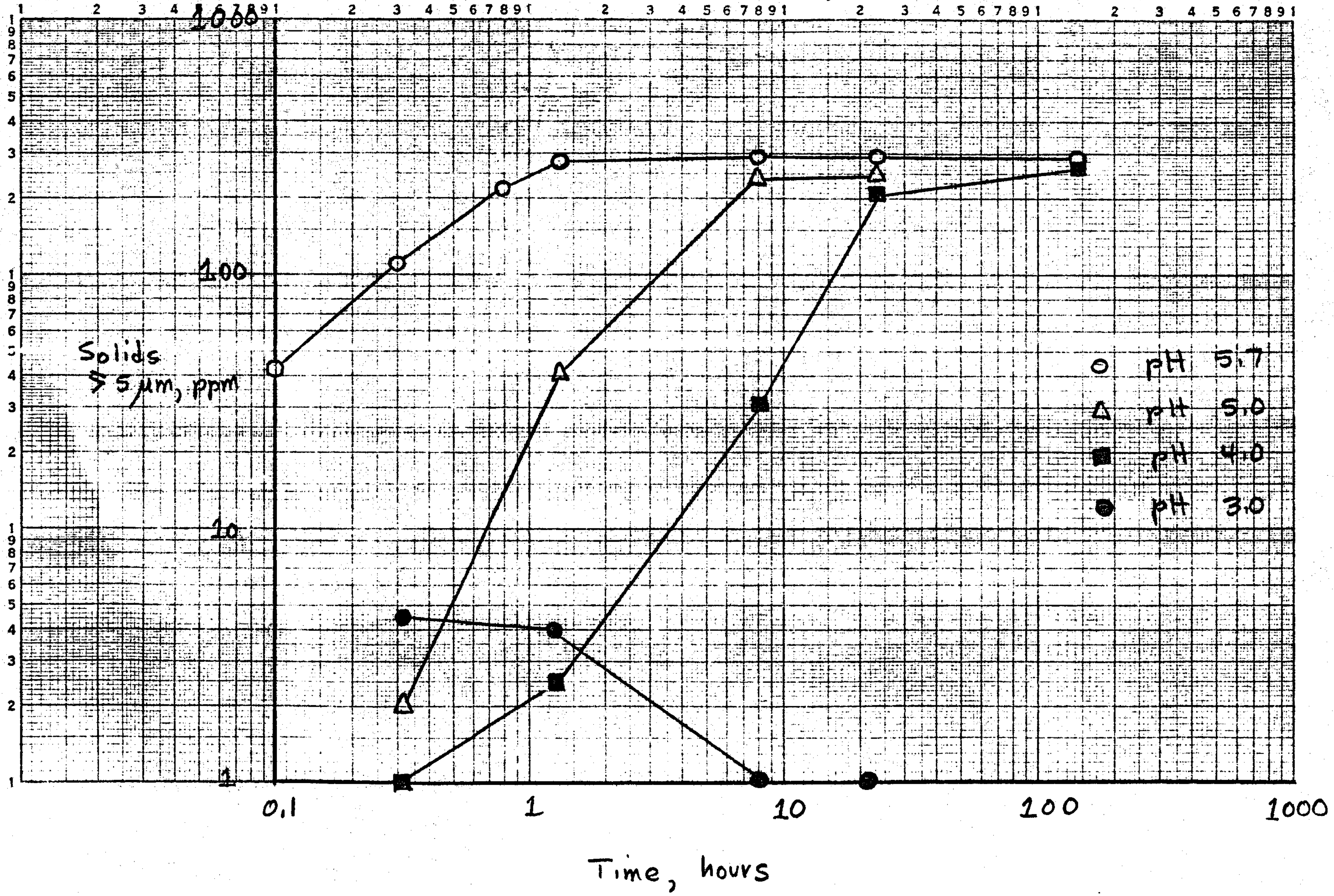


Figure 1. Concentration of Silica in Filtered Brine vs. Time after Flashing to 105°C. (Brine incubated at 90 ±5°C)

Figure 2. Concentration of Filterable Solids in Brine vs. Time after Flashing to 105°C.
(Brine incubated at 90 ± 5°C)



Each of a series of samples of brine was also diluted ∿20% by weight with pure water to test this approach to controlling solids precipitation. These samples are being examined only at periods longer than 24 hr, and the data obtained are summarized in Table 2. Although these experiments are not yet complete, it appears that the water dilution has some effect, especially at pH 4, in keeping the SiO_2 in solution for a longer time and in significantly reducing the quantity of solids >5 μm in size. Note in these data that the dilution itself immediately reduces the concentrations by a factor of 0.8.

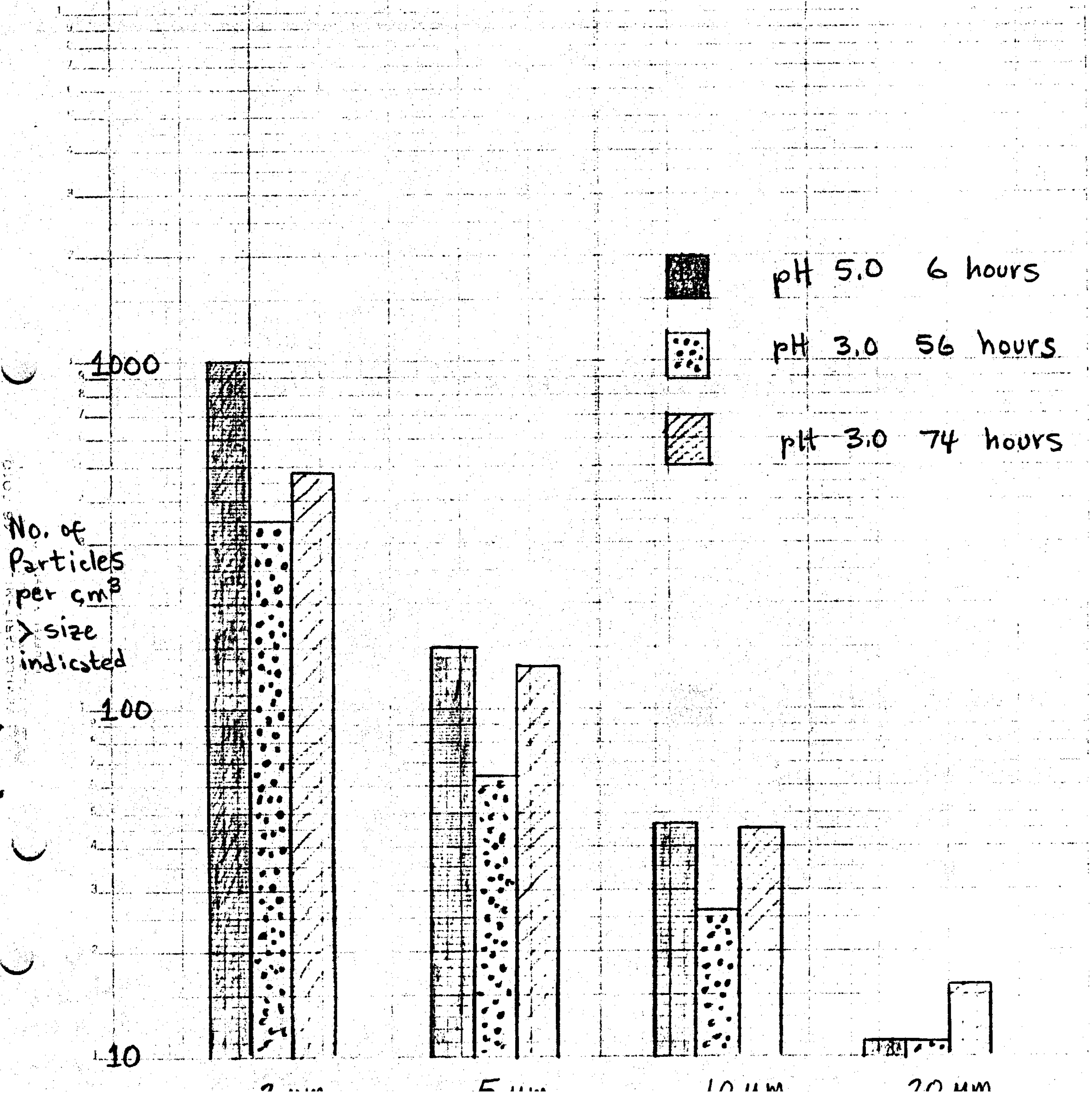
Table 2. Effect of dilution of brine with water (∿20% w/w) on formation of solids and retention of SiO_2

		Undiluted Brine		Diluted Brine	
		SiO_2, ppm	Solids, ppm	SiO_2, ppm	Solids, ppm
ph 5.7	24 hr	201	286	244	234
	144 hr	185	292	200	201
pH 5.0	24 hr	267	229	286	49
	164 hr	172			
pH 4.0	24 hr	273	219	349	17
	144 hr	181	278	315	19
pH 3.0	24 hr	452	1	385	0
	218 hr	260		363	

Several attempts (with L. B. Owen) were also made to measure the size distribution of suspended particles in the brine using a relatively new device manufactured by the Spectrex Corp., the model ILI 1000 laser particle counter. This instrument scans the solution with a laser beam and reads out the number of particles per ml larger than a given threshold size. It appeared to be most useful when the fluid tested did not have visible turbidity. If it did, or if the particle size was larger than ∿50 μm, the instrument was not applicable.

Data on three solutions examined are summarized in Figure 3. The pH 5 solution was at a point in time when filtration was very difficult (a stage through which all brines pass, being easy to filter either before or after). The distribution of particles in the vicinity of 5 μm lends credence to our conjecture that the difficulty in filtering is due to a match between the particle size and

Figure 3. Solid particle size distribution in brines



the filter crucible pore size. The pH 3 solution was visually clear both times it was measured, but the data show that the particles in this solution are still growing. Measurements such as these might provide a good early-warning indication of the performance of effluent treatment procedures, particularly because the instrument could be operated on-line.

The pH values of the various brines incubated for >1 week are being measured, since this is germane to the possible mechanisms of solids precipitation. In each case the pH has decreased: pH 5.7 to 4.8 and pH 4.0 to 3.4. It is beyond the scope of this report to discuss this in detail, but most solid-formation reactions that have been postulated[2] do increase the concentration of H^+ ion.

Acknowledgements

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1. J. H. Hill, C. H. Otto, Jr., C. J. Morris, R. Quong, and L. B. Owen, in The LLL Geothermal Energy Program Status Report, January 1976 to January 1977, Lawrence Livermore Laboratory Rept. UCRL-50046-76 (1977), pp. 94-98.
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