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CHEMICAL BEHAVIOUR OF GEOTHERMAL SILICA AFTER PRECIPITATION
FROM GEOTHERMAL FLUIDS WITH INORGANIC FLOCCULATING AGENTS
AT THE HAWAII GEOTHERMAL PROJECT WELL-A (HGP-A)

A REPORT PREPARED FOR THE
HAWAII NATURAL ENERGY INSTITUTE
OF
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AND
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INTRODUCTION

The report presented herein summarizes the results of experiments carried out during the period July 1985-June 1986 at the Hawaii Geothermal Project Well-A (HGP-A). The experiments performed are a continuation of previous work dealing with the problem of removal of waste-silica from spent fluids at the experimental power generating facility in the Puna District of the island of Hawaii.

Geothermal discharges from HGP-A represent a mixture of meteoric and seawaters which has reacted at depth with basalts from the Kilauea East Rift Zone under high pressure and temperature (Thomas, 1982). The well which was completed in 1976 was tested intermittently between 1976 and early 1981, and has been under commercial production since March 1982. The geothermal fluid from the well is composed of approximately 43% steam and 57% liquid. The unflashed brine (at the well-head) is nearly 0.3 M in NaCl, and is highly enriched over its seawater component in Ca, K, Li, and SiO₂(aq) (De Carlo and Thomas 1985). The bottom hole temperature of 350 degrees Celsius leads to basalt/water interactions resulting in a dissolved silica concentration between 800 and 900 mg/L governed not by the extent of seawater intrusion into the system but by the amorphous solubility of silica at the equilibration temperature (Fournier and Rowe, 1966; Iler, 1979). Analysis of the brine has shown that although the concentration of metal ions contributed by the seawater component of the geothermal fluid has increased (indicating a higher seawater influx to the geothermal system, the silica content has remained nearly constant since the beginning of production at the well thus confirming both the origin and controlling mechanism mentioned above.

After separation of the steam phase of the geothermal fluid from the liquid phase and a final flashing stage to 100 degrees Celsius and atmospheric pressure, the concentration of the silica increases to approximately 1100 mg/L. This concentration represents five to six times the solubility of amorphous silica in this temperature range, and the silica remains in a metastable state (colloidal suspension ?) which precipitates at a very slow rate. The high silica content results in a slow deposition of significant amounts of scale both in pipes and conduits, as well as in the final settling ponds thus contributing to a long-term clogging problem. Although alternative brine disposal methods such as reinjection of the fluids at depth under pressure and secondary use of the fluids in heat exchangers have been considered at HGP-A and will most likely be necessary should the power producing facilities be expanded, these techniques are presently not feasible due to the problems associated with silica scale.

We have evaluated and successfully developed bench scale techniques utilising adsorptive bubble flotation for the removal of colloidal silica from the spent brine discharge in the temperature range of 60-90 degrees C. The methods employed resulted in recovery of up to 90% of the silica present above its amorphous solubility in the experimental temperature range studied. The

results of this work are currently in press in the journal Separation Science and Technology. As a continuation of this work we wished to more closely examine the chemical characteristics of the silica flocculated by the addition of ferric and aluminum salts. This report thus only presents data dealing directly with the chemical characterization of naturally and artificially precipitated silica flocs. A copy of the manuscript in press is also appended.

Motivation for the chemical characterization of the precipitated silica arose from the potential of utilizing the material for secondary applications. It is of interest then to understand the nature of the relationship between metals added to flocculate the silica, certain brine constituents which are known to be incorporated into the silica scale under natural conditions, and the silica itself. The strength of the bonds (if any) between these various species and the ease (or difficulty) of removal of the metals (which may prove to be contaminants in specific applications) from the silica need to be evaluated.

EXPERIMENTAL

Flocculation of the meta-stable colloidal silica present in the brine discharge was achieved by the addition of small amounts of ferric sulfate, aluminum sulfate, or potassium aluminum sulfate (alum) to specified amounts of the brine discharge collected in insulated containers. Due to the acidic nature of the metal solutions added, the pH of the brine was readjusted to pH 8 which is near the natural range (pH 7.4-7.8) for the brine discharge. Insulated vessels were used throughout the experiments in order to minimize temperature-drop induced flocculation of the silica. Thomas (unpublished data 1986) has reported that up to 50% of the reactive silica settles out of solution (upon cooling to room temperature) within a period of two hours and up to 70% within 18-20 hours after collection from the discharge point. Concentrations of the added salts ranged from 6.1×10^{-5} mole to 5.0×10^{-4} mole trivalent metal ion per liter of brine. Silica was also precipitated without the addition of metal salts by simply raising the pH of the brine to near pH 9. In all cases the flocculated silica was allowed to settle to the bottom of the reaction vessel, the mother solution decanted off (after removal of an aliquot for residual silica analysis), and the remaining slurry collected for subsequent treatment. Removal of a large portion of the remaining water was achieved by centrifugation and decantation. The physical appearance of the precipitated matter at this point was that of a gel with the color dependent upon the metal ion used in the flocculation. Drying of the samples was not carried out until return to the U.H. Manoa campus.

Selective leaching was carried out on the samples of silica precipitated by the methods described above. The leachings were performed in two different sets of experiments. The first consisted of rinsing the precipitates with water to remove any remaining entrapped geothermal fluids followed by further centrifugation; three splits of the gel obtained in such a manner were then taken. The first portion was kept without further treatment, the second was washed with approximately 50 mL of 0.146 M HCl manually agitated, centrifuged and then rinsed with water prior to storing, and the third washed with 2.0 M HCl in a manner analogous to the second split. The second method which was used in a much more widespread manner consisted of taking an accurately weighed split of unwashed (unrinsed) silica which was previously dried to a constant weight at 110 degrees C in an oven and subjecting it to serial leachings with 20 mL portions of distilled water, then with increasingly concentrated 20 mL portions of HCl. Concentrations employed were 0.05, 0.10, 0.15, 0.20, 0.35, 0.50, and 2.0 M HCl. Leaching of the samples was performed

by manual agitation for a period of five minutes, followed by separation of solid and aqueous phases by centrifugation and rinsing with distilled water. Solid residues from the leaching with a given concentration of acid were subjected to subsequent steps with the last residue stored for any further work. All leach solutions and associated water rinses were transferred to volumetric flasks upon decantation after centrifugation, and were diluted to 50 mL with 1.0 or 2.0 M HCl for atomic spectrometric analysis.

Triplicate splits of the original precipitates collected or generated at HGP-A were prepared for elemental analysis by solubilization with mineral acids in a high pressure Parr bomb using a slight modification of methods previously described by De Carlo et al. (1982).

Atomic spectrometric analyses of the precipitates were performed using a Leeman Labs Plasma Spec I Inductively Coupled Plasma Atomic Emission Spectrometer (ICP/AES) system by accepted methods. Standard reference solutions containing the metals of interest (Al, Ca, Fe, Mg, and Na) were prepared from commercially obtained concentrated single element standard solutions and mixed in a matrix matching that of the precipitates. The instrument was calibrated and samples compared to the calibration curves. The relative precision of the analyses is to $\pm 5\%$ for all metals except Na where it is on the order of $\pm 10\%$. Potassium (K) analyses were performed by flame atomic emission spectroscopy using a Perkin-Elmer Model 603 double beam instrument with a relative precision of $\pm 5\%$. Copper and lead were also analyzed in selected samples of silica precipitated from un-flashed brine by furnace atomic absorption spectrometry (FAAS). Leach liquors were also analyzed for the metals of interest by ICP/AES and FAAS in a manner analogous to that for the digested precipitates.

RESULTS

Chemical Composition of Silica Precipitates.

The results of elemental analyses of the silica precipitated from flashed brine under a variety of conditions are presented in Table 1. These data show an increased content in the metal added as a flocculating agent as a function of larger additions of the metal salt solution per liter of brine. These data are also presented graphically in Figures 1 through 3. In general the results are not surprising, however there are some significant unexpected changes in the metal incorporation at higher concentrations of flocculating agent. Of particular interest is the fact that the amount of Ca incorporated into the silica seems to drop above an addition of 4.0×10^{-4} M ferric ion or aluminum from alum, but does not exhibit this behavior when aluminum as the single metal sulfate is added above this concentration level. This would seem to indicate that the Fe or Al is replacing Ca in the silica structure or preventing its incorporation simply from a mass action standpoint. Why such behavior is not exhibited when using aluminum sulfate remains unknown. We also note an increase in the Al content of the precipitated silica above an added Fe concentration of 3.0×10^{-4} M. The increased incorporation of Al result from changes in the silica surface charge characteristics upon adsorption of large amounts of Fe hydroxy complexes. Silica and Fe hydroxides have isoelectric points near pH 2.5 and 6.5 respectively (Parks, 1965); addition of further Fe hydroxides may increase the number of negatively charged sites at pH 8.0. In such a case, Al hydroxy complexes which are still positively charged at pH 8.0 (Parks, 1965) will be more efficiently scavenged from solution. Mg and Na contents of the silica do not appear to change significantly with changing concentrations of flocculating agent added but appear

TABLE 1

GEOTHERMAL SILICA SAMPLES - ELEMENTAL ANALYSIS

SAMPLE	PREPARATION #	Ca (mg/g)		Mg (mg/g)		Na (mg/g)		Al (mg/g)		Fe (mg/g)	
		avg	s.d.	avg	s.d.	avg	s.d.	avg	s.d.	avg	s.d.
FI-84-1B	5.0X10E-4 M Fe	11.7	0.2	0.025	0.006	116.20	11.30	4.76	1.66	21.56	0.59
FI-84-2	4.0X10E-4 M	15.2	0.8	0.024	0.001	143.70	7.60	6.51	1.76	12.90	0.69
FI-84-3	3.0X10E-4 M	14.7	0.1	0.014	0.002	128.20	2.00	0.23	0.02	10.38	0.39
FI-84-4	2.5X10E-4 M	16.0	0.2	0.018	0.005	135.33	0.94	0.19	0.08	8.83	0.10
FI-84-5	2.0X10E-4 M	14.6	0.4	0.018	0.001	120.80	0.05	0.20	0.14	7.75	0.08
FI-84-6	1.5X10E-4 M	14.7	0.2	0.027	0.009	123.10	1.70	0.24	0.09	5.75	0.12
FI-84-7	1.0X10E-4 M	14.7	0.5	0.011	0.001	125.67	6.56	0.10	0.13	3.62	0.11
FI-84-8F	5.0X10E-4 M KAl	10.6	0.3	0.020	0.016	49.90	0.34	13.25	0.43	0.14	0.09
FI-85-1	4.0X10E-4 M	18.8	0.2	0.013	0.004	167.60	1.90	5.66	0.27	n.d.	
FI-85-2	3.0X10E-4 M	16.4	0.2	0.015	0.008	158.00	1.78	4.68	0.24	0.14	0.10
FI-85-2A	2.5X10E-4 M	14.1	0.0	0.006	0.002	137.90	3.10	5.00	0.07	n.d.	
FI-85-2B	2.0X10E-4 M	16.9	0.6	0.018	0.002	134.40	7.39	3.87	0.11	n.d.	
FI-85-2C	1.5X10E-4 M	16.9	0.4	0.011	0.002	143.60	3.76	2.62	0.03	n.d.	
FI-85-2D	1.0X10E-4 M	12.7	0.3	0.013	0.001	102.20	1.40	2.59	0.21	n.d.	
FI-85-3	5.0X10E-4 M Al	15.2	0.4	0.008	0.001	145.30	4.09	9.28	0.35	n.d.	
FI-85-4	4.0X10E-4 M	14.6	0.4	0.006	0.001	148.40	6.71	6.95	0.00	n.d.	
FI-85-5	3.0X10E-4 M	16.4	0.2	0.011	0.001	163.90	5.10	4.65	0.14	n.d.	
FI-85-6	2.5X10E-4 M	14.3	0.3	0.005	0.000	152.30	1.88	4.51	0.12	n.d.	
FI-85-7	2.0X10E-4 M	14.2	0.5	0.007	0.001	145.50	10.16	5.30	0.85	n.d.	
FI-85-8	1.5X10E-4 M	13.2	0.2	0.005	0.001	139.90	4.00	3.06	0.16	n.d.	
FI-85-9	1.0X10E-4 M	15.1	0.6	0.006	0.002	152.60	2.07	0.90	0.07	n.d.	
LEACH METHOD											
FI-90-1	dd water #	4.7	0.4	0.007	0.003	2.74	0.10	0.27	0.11	4.46	0.01
FI-94-1A	0.146M HCl	1.3	0.0	0.004	0.001	0.53	0.13	0.16	0.02	3.06	0.01
FI-94-1B	2M HCl	1.4	0.0	0.011	0.002	0.16	0.10	0.12	0.00	0.18	0.02
FI-93-1	dd water \$	5.7	0.0	0.032	0.000	6.28	0.07	0.29	0.02	8.32	0.02
FI-93-2A	0.146M HCl	1.4	0.0	0.020	0.000	0.19	0.03	n.d.		3.10	0.02
FI-93-2B	2M HCl	1.2	0.2	0.023	0.001	0.10	0.02	0.31	0.02	0.09	0.00
FI-91-2	1.75X10E-4 M Fe	5.0	0.1	0.001	0.004	12.90	0.45	0.20	0.03	5.42	0.02
FI-94-2	2.5 X10E-4 M	5.9	0.1	0.012	0.001	17.20	0.30	n.d.		7.95	0.20
FI-95-1	1.25X10E-4 M	5.3	0.1	0.026	0.002	14.33	0.07	0.20	0.01	5.22	0.18

n.d. None detected.

Original preparation of samples with 2.5 X 10E-4 M Fe added.

\$ Original preparation of samples with 1.25 X 10E-4 M Fe added.

Samples below are from unflashed brine.

Alum prep * see	7.8	0.3	56.70	2.91	41.10	0.45	14.50	0.10	0.126	0.012
Fe prep below	7.1	0.1	47.80	6.24	15.10	0.06	0.283	0.018	16.80	0.06

*Alum prep: 3 ml 0.1 M Al(III) in 500 mL water added to 1L unflashed brine, precipitate washed twice with DD water.

Iron prep: 3 mL 0.1 M Fe(III) in 500 mL water added to 1L unflashed brine, precipitate washed twice with DD water.

COMPOSITION OF SILICA UNFLASHED BRINE

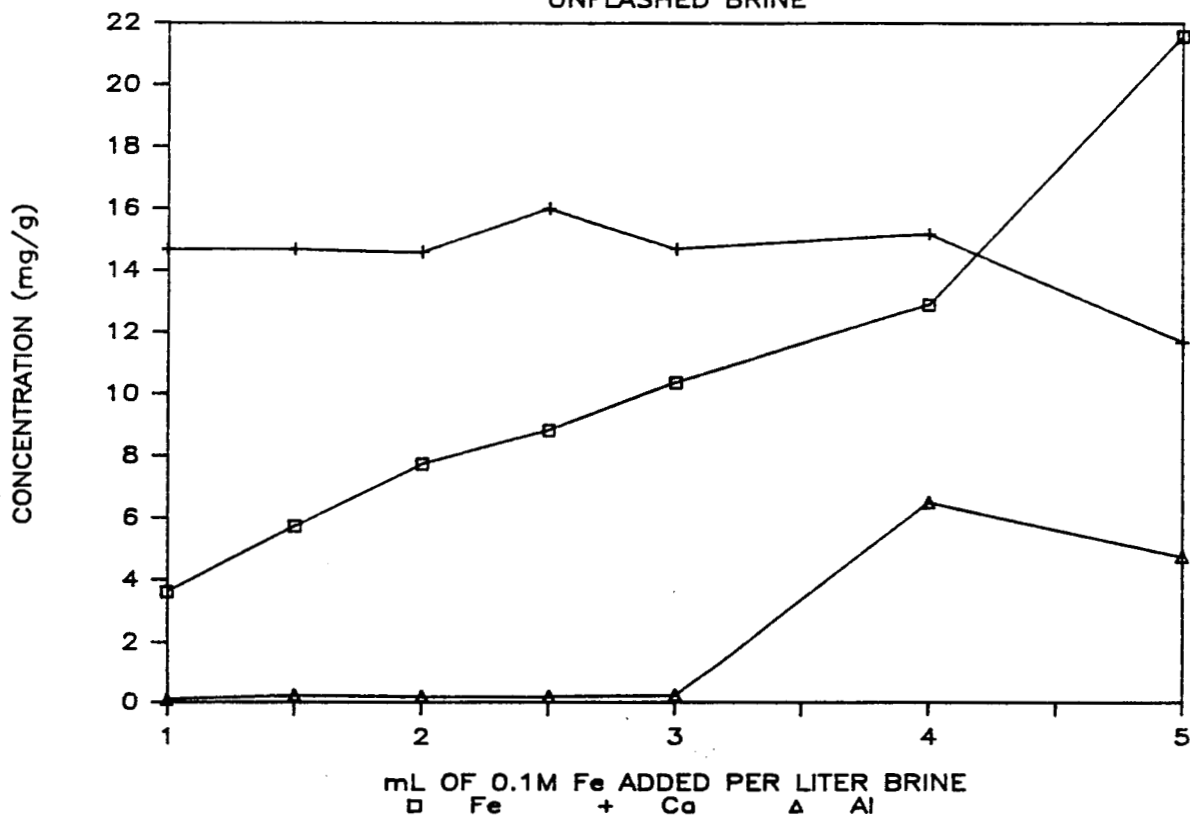


FIGURE 1: COMPOSITION OF SILICA PRECIPITATED FROM FLASHED GEOTHERMAL BRINE BY THE ADDITION OF FERRIC SULFATE AS A FUNCTION OF IRON CONCENTRATION EXPERIMENTS CARRIED OUT AFTER pH ADJUSTMENT TO pH = 8.0

COMPOSITION OF SILICA UNFLASHED BRINE

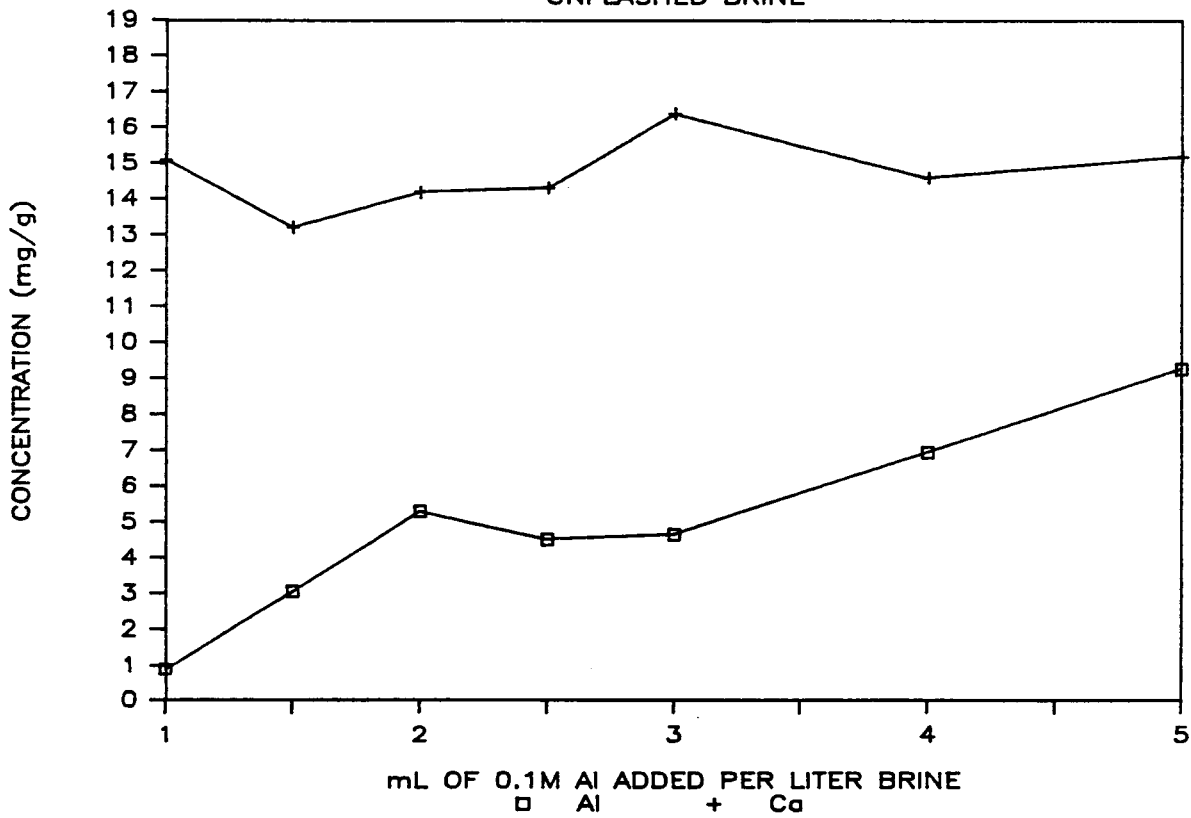


FIGURE 2: COMPOSITION OF SILICA PRECIPITATED FROM FLASHED GEOTHERMAL BRINE BY THE ADDITION OF ALUMINUM SULFATE AS A FUNCTION OF ALUMINUM CONCENTRATION EXPERIMENTS CARRIED OUT AFTER pH ADJUSTMENT TO pH = 8.0.

COMPOSITION OF SILICA UNFLASHED BRINE

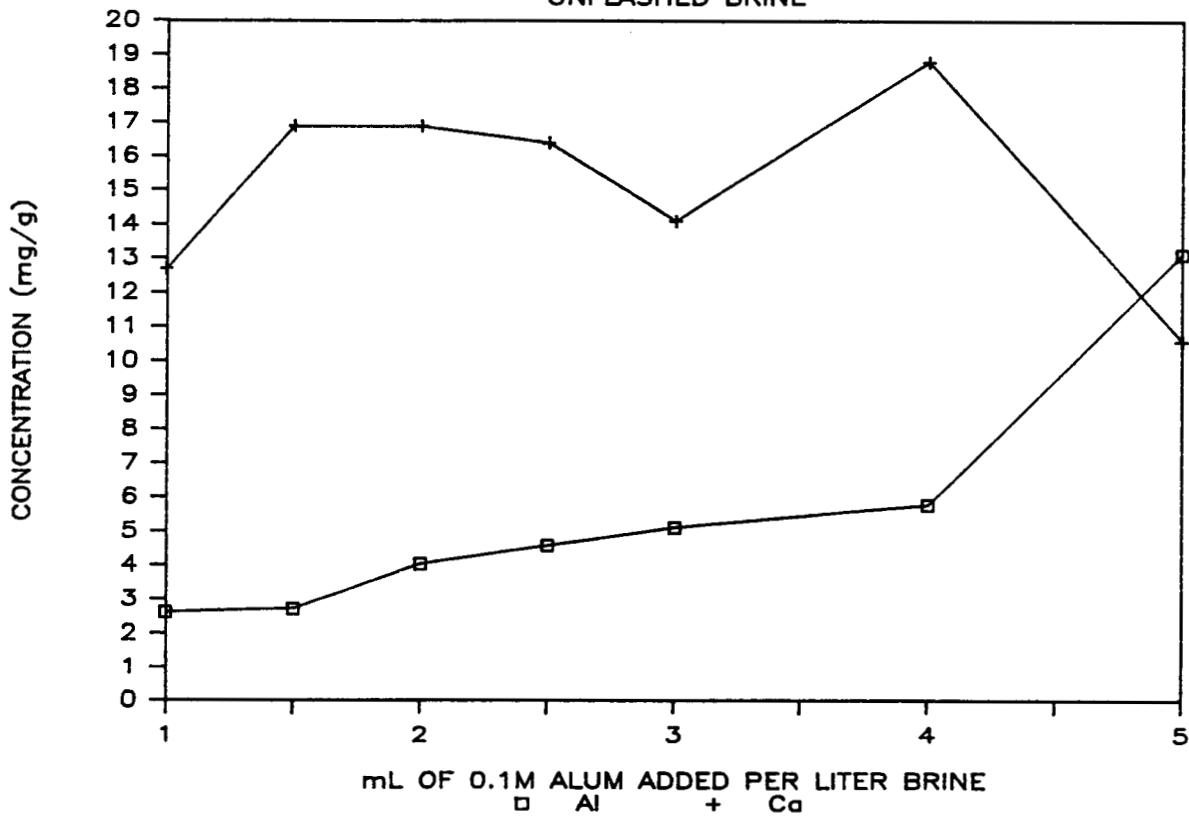


FIGURE 3: COMPOSITION OF SILICA PRECIPITATED FROM FLASHED GEOTHERMAL BRINE BY THE ADDITION OF ALUM (POTASSIUM ALUMINUM SULFATE) AS A FUNCTION OF ALUMINUM CONCENTRATION. EXPERIMENTS CARRIED OUT AFTER pH ADJUSTEMENT TO pH = 8.0

to reflect simply an incorporation of the amount of these metals present in the brine at the time of precipitation. Whether these metals are simply adsorbed onto or chemically bound to the silica is the subject of a discussion in the leaching experiments. Also included in Table 1 are the results of the first set of leachings carried out at HGP-A on separate splits of the high water content silica. The results indicate that the Na in the silica is simply an entrapped residue from the brine since its concentration decreases from greater than 13% w/w to less than 0.3% just by rinsing the precipitate with distilled water (see sample FI-84-4 versus 90-1 in Table 1). The concentration of Ca in the precipitate is also much lower in the water rinsed (FI-90-1) than in the unrinsed sample (FI-84-5), but decreases further upon washing with 0.146 M HCl. From these observations it appears that Ca is more tightly bound to the silica surface than Na. Due to the divalent nature of the Ca ion it is expected to have a greater attraction for the negatively charged silica surface than the univalent Na ion. Similar observations can be made with the sample prepared using lesser additions of ferric sulfate (see Figures 4 and 5). Examination of these figures reveals that both Ca and Fe achieve a nearly identical concentration in the samples after the leaching independent of the amount of Fe initially added as a flocculant.

Selected elemental analyses for five other silica precipitates are given in Table 2. These data are for natural silica scale from two locations, and silica precipitated by addition of either NaOH to spent brine or metallic flocculating agents to unflashed brine.

Physical Description of Silica Precipitates

It is of interest to note that the silica prepared by different methods (by enhanced flocculation or by natural deposition) seems to form in a variety of particle sizes. Although no particle size determinations were carried out other than those performed outside the institute, we note a significant range of sizes in the various precipitates as observed by a layering which occurs during centrifugation of the samples following leaching. It is possible that the size distribution changes as a result of leaching but this is probably not the main factor governing particle size. In the case of silica which had precipitated naturally in the conduits of the power plant prior to the flashing stage the layering was particularly obvious. After the leaching steps culminating with 2.0 M HCl, three distinct zones were observed. The top layer which comprises the finest size fraction was quite dark and resembled a clay mineral, the second zone which is also quite fine was not as dark and was grey in color, the third layer was quite coarse and seems to consist of two phases: one yellow very much like elemental sulfur, the other more like coarse sand. Other samples of naturally deposited silica also exhibited some size fractionation but with no significant color zonation. Samples which were precipitated by the addition of ferric ion however seemed to lose color more readily (i.e. leached free of Fe) from the finer fractions. This may be a result of a greater surface area available for attack in the case of the fine particulates as opposed to the coarse fraction. Another particularly notable physical property of the silica precipitated with iron is a higher settling rate from the brine after flocculation as compared to silica precipitated either with alum or with aluminum. This behavior may result from differing surface charge characteristics. Parks (1965, 1967) has noted that mixed precipitates exhibit an isoelectric point (iep) between that of the pure major phase and that of the contaminating phase. In light of this behaviour it would be anticipated that the aluminum bearing silica would have iep shifts towards higher pH ($\text{pH}(\text{iep}) \text{Al}(\text{OH})_3 = 9.2$) thus reducing its surface charge and its ability to coagulate relative to iron bearing silica ($\text{pH}(\text{iep}) \text{Fe}(\text{OH})_3 = 8$) and result in slower settling rates. Such behaviour may be of importance in silica recovery schemes which would depend upon natural settling of the flocs.

TABLE 2
CHEMICAL COMPOSITION OF SILICA SCALE FROM HGP-A GEOTHERMAL FLUIDS

Sample @	Element in mg/kg					
	Na	K	Ca	Mg	Fe	Al
X-29-1	3.78 #	5760	39.6 #	60	n.d.	n.d.
X-29-2	1580	850	2480	93	750	n.d.
X-29-3	2010	926	12050	1385	1.02 #	2100
X-29-4	1.51 #	n.d.	7080	48	1.68 #	14
X-29-5	4.11 #	n.d.	7800	57	4.11 #	1.45 #

n.d. Not Determined.

Expressed as weight percent.

@ Origin of samples:

X-29-1 silica precipitated after addition of NaOH to discharge fluids.

X-29-2 silica deposited by natural precipitation in the atmospheric flash tank.

X-29-3 silica scale deposited by natural precipitation at the turbine nozzle inlet.

X-29-4 silica precipitated by addition of 2.5×10^{-4} M Fe(III) to unflashed brine at pH 8.0.

X-29-5 silica precipitated by addition of 2.5×10^{-4} M "Alum" to unflashed brine at pH 8.0.

COMPOSITION OF LEACHED SILICA UNFLASHED BRINE (1.25type)

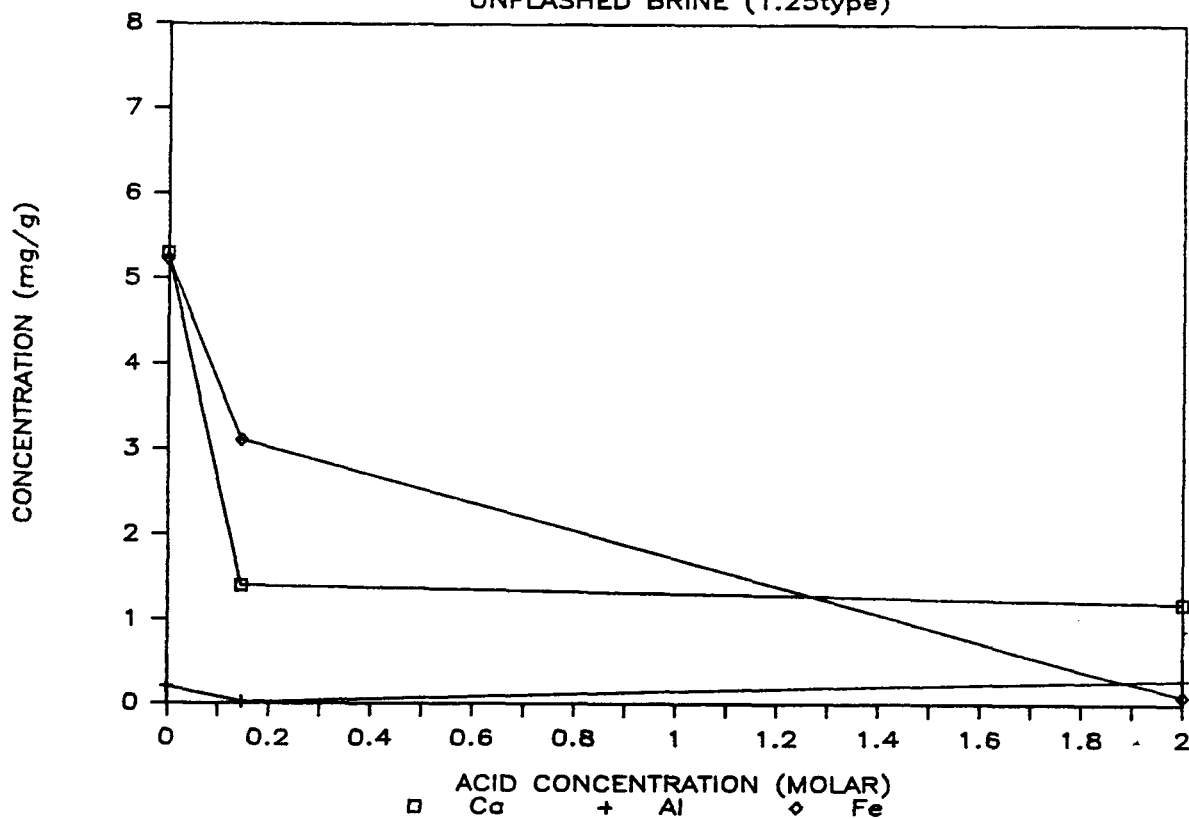


FIGURE 4: COMPOSITION OF SILICA AFTER LEACHING WITH HYDROCHLORIC ACID OF VARYING CONCENTRATION. SILICA ORIGINALLY PREPARED BY ADDITION OF 1.25 mL of 0.1 M Fe(III) PER LITER OF FLASHED GEOTHERMAL BRINE AND ADJUSTED TO pH = 8.0
FOR COMPARISON SEE IN TABLE 1 SAMPLE FI-85-6,7 (UNRINSED)
DATA POINTS CORRESPOND TO SAMPLES FI-93-1,2a,2b

COMPOSITION OF LEACHED SILICA UNFLASHED BRINE (2.5type)

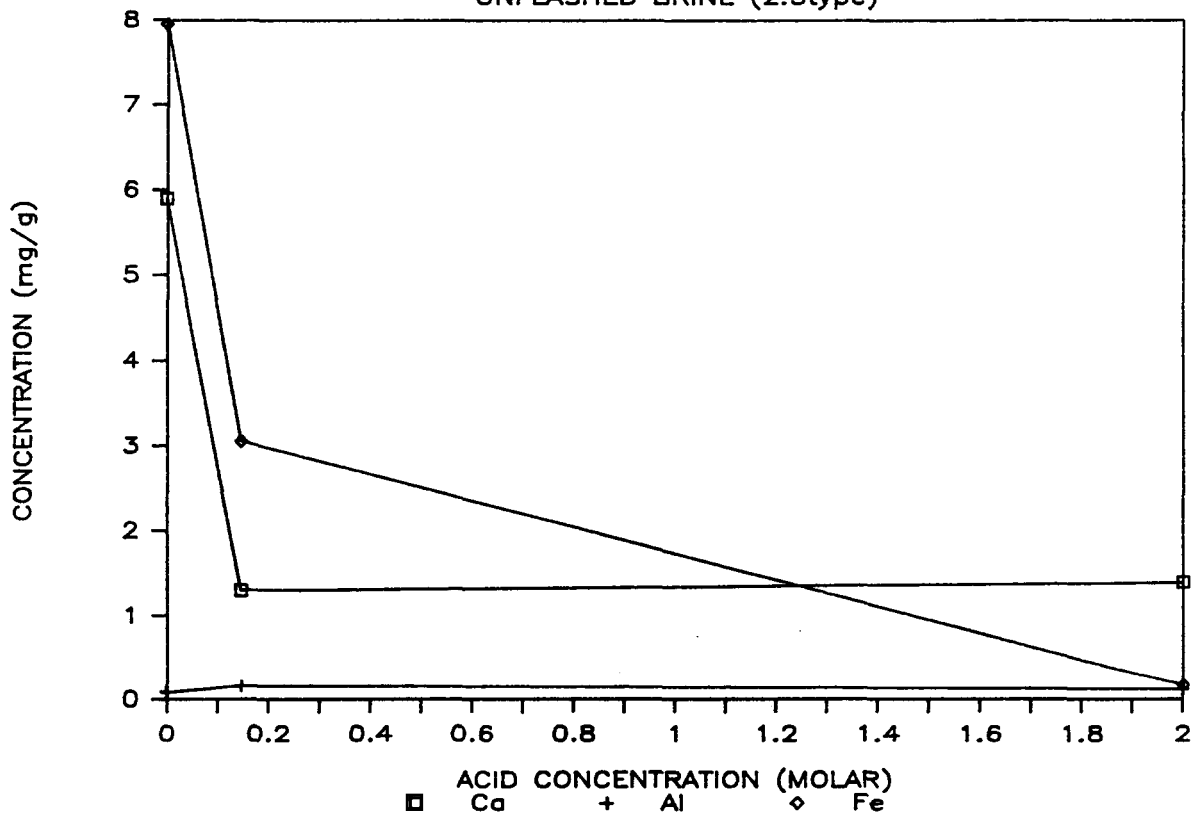


FIGURE 5: COMPOSITION OF SILICA AFTER LEACHING WITH HYDROCHLORIC ACID OF VARYING CONCENTRATION. SILICA ORIGINALLY PREPARED BY ADDITION OF 2.50 mL OF 0.1 M Fe(III) PER LITER OF FLASHED GEOTHERMAL BRINE AND ADJUSTED TO pH = 8.0 FOR COMPARISON SEE IN TABLE 1 SAMPLE FI-85-4 (UNRINSED) DATA POINTS CORRESPOND TO SAMPLES FI-90-1, FI-94-1a, 1b

Settling velocities of the precipitates could be altered by changes in pH (i.e. changes in surface charge characteristics), and may be used to advantage in certain instances. In this case it appears that use of Fe as the flocculating agent allows rapid settling without raising the pH of the fluids above pH = 8, whereas use of Al would require a pH significantly above pH = 9; the choice of flocculating agent then becomes a matter of which metal is preferable in the final product. Selected zeta potential measurements are given in Table 3.

Serial Leaching Experiments

The following section presents the results of comprehensive leaching experiments carried out on the silica precipitates. These include both those prepared by enhanced flocculation and those which had accumulated naturally as silica scale at various locations of the HGP-A plant. The data are discussed on the basis of the metal of interest for all samples. Thus each subsection compares leaching behaviour as a function of physical and chemical properties of the samples. The metals Al and Fe are covered first as they were utilised to generate the majority of the samples. Their importance though does not arise from their concentration in the silica as other elements studied can be present in much larger quantities. The alkali metals K and Na are the second group discussed, and the alkaline earths Mg and Ca last. The data from the leaching experiments are presented in Tables 4-9; these appear individually in the appropriate sections dealing with the metals studied.

Aluminum:

Samples which were precipitated by the addition of aluminum sulfate or alum are quite similar in terms of the shape of the cumulative removal curves for Al. The cumulative amounts of Al removed upon leaching for samples FI-84-8 through 85-9 are shown in Figures 6-8. Comparing the data to those in Table 1 (representing the original concentration of Al in the silica), it is apparent that only approximately 25-74% of the silica is readily removed by the HCl leaching and that most of that amount is very loosely held by the silica (as evidenced by removal with less than 0.5 M HCl). The remaining Al is much more tightly bound (not leached by 2.0 M HCl) and may represent Al involved in cross linking of the silica structure in a manner analogous to that suggested by De Carlo and Ronay (1986) in the case of Fe. A similar pattern of Al removal is evident in sample X-29-5 which was prepared by the addition of alum to unflashed geothermal fluid (see Figure 9a). Another sample of interest in terms of Al leaching behavior is X-29-4; the silica was precipitated from unflashed brine by the addition of ferric sulfate. The shape of the removal curve shown in Figure 9b indicates that the small amount of Al incorporated in the silica is primarily physically adsorbed (thus quite labile). The shape of the curve is quite reminiscent of those in Figures 6-8. It is probable that the amount of Al initially incorporated is not only a function of the amount added to the brine but that kinetics also control the total concentration of the metal in the silica (Thomas pers. comm. 1986). This kinetic effect may be even more severe in the leaching experiments where the time of contact between the HCl and silica partially controls the amount of metal removed. Samples precipitated with alum have a final concentration ranging from 1.7 mg/g to nearly 3.5 mg/g Al after leaching with the various HCl solutions. If the remaining amount of Al is representative of that tied up in bridging sites, one would expect nearly identical Al levels in all the samples. The factor of three difference thus may be a result of insufficient leaching contact between the silica and HCl.

Samples recovered by enhanced flocculation in the presence of Fe (e.g. FI-84-1 through 84-7) or naturally deposited silica (X-29-2 and 29-3) have

TABLE 3
ZETA POTENTIALS OF FLOCS GENERATED FROM TREATMENTS OF
HGP-A FLASHED BRINE #

Flocculant	none	Fe(III)	Fe(III)	Fe(III)	NaOH	Fe(III) @
Zeta Potential (in mV)	-45+/-3	-39+/-2	-36+/-2	-27	-9+/-3	-38
Molarity of Fe	0	5.3X10E-5	1.3X10E-4	2.6X10E-4	0	2.0X10E-3
pH	7.7	8.0	8.0	8.0	>9.0	8.0

Ambient temperature, 67-100 V applied potential, 30-40 mMho/cm conductivity
1.8 X 10 E-2 M silica.

@ From De Carlo and Thomas (1986), 6.5 X 10 E-3 to 8.2 X 10 E-3 M silica.

TABLE 4

CUMULATIVE REMOVAL OF Al FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.20	0.50	2.00
	Concentration of Al (in ppm)						
FI-85-3		2360.00	4040.00	427.00	599.00	197.00	357.00
cum.		2360.00	6400.00	6827.00	7426.00	7623.00	7980.00
original							9400.00
FI-85-4	232.00	943.00	2400.00	1040.00	677.00	505.00	513.00
cum.	232.00	1175.00	3575.00	4615.00	5292.00	5797.00	6310.00
original							6950.00
FI-85-5	225.00	555.00	1170.00	452.00	416.00	297.00	379.00
cum.	225.00	780.00	1950.00	2402.00	2818.00	3115.00	3494.00
original							4700.00
FI-85-6	215.00	828.00	1470.00	495.00	428.00	279.00	326.00
cum.	215.00	1043.00	2513.00	3008.00	3436.00	3715.00	4041.00
original							4480.00
FI-85-7	216.00	698.00	876.00	313.00	264.00	262.00	252.00
cum.	216.00	914.00	1790.00	2103.00	2367.00	2629.00	2881.00
original							5330.00
FI-85-8	316.00	753.00	496.00	296.00	300.00	211.00	124.00
cum.	316.00	1069.00	1565.00	1861.00	2161.00	2372.00	2496.00
original							3230.00
FI-85-9	343.00	355.00	282.00	71.60	56.70	49.30	91.40
cum.	343.00	698.00	980.00	1051.60	1108.30	1157.60	1249.00
original							1900.00
X-29-1		33.60	212.00	789.00	432.00	637.00	214.00
cum.		33.60	245.60	1034.60	1466.60	2103.60	2317.60
X-29-2		66.90	19.50	20.10	18.30	12.90	22.60
cum.		66.90	86.40	106.50	124.80	137.70	160.30
X-29-3		194.00	63.00	77.50	47.60	40.50	86.40
cum.		194.00	257.00	334.50	382.10	422.60	509.00
X-29-4		67.80	67.80	11.80	7.70	2.30	11.80
cum.		67.80	135.60	147.40	155.10	157.40	169.20
X-29-5		378.00	378.00	2400.00	748.00	278.00	660.00
cum.		378.00	756.00	3156.00	3904.00	4182.00	4842.00

Figure 6. Cumulative removal of Al from silica prepared by the addition of 5×10^{-4} $\text{KAl}(\text{SO}_4)_2$ as a function of HCl concentration.

Figure 7. Cumulative removal of Al from silica prepared by the addition of $\text{KAl}(\text{SO}_4)_2$ as a function of HCl concentration.

- a. FI-85-1: 4.0×10^{-4} M Al
- FI-85-2: 3.0×10^{-4} M Al
- FI-85-2A: 2.5×10^{-4} M Al

- b. FI-85-2B: 2.0×10^{-4} M Al
- FI-85-2C: 1.5×10^{-4} M Al
- FI-85-2D: 1.0×10^{-4} M Al

Figure 8. Cumulative removal of Al from silica prepared by the addition of $\text{Al}_2(\text{SO}_4)_3$ as a function of HCl concentration.

- a. FI-85-3: 5.0×10^{-4} M Al
- FI-85-4: 4.0×10^{-4} M Al
- FI-85-6: 2.5×10^{-4} M Al

- b. FI-85-5: 3.0×10^{-4} M Al
- FI-85-7: 2.0×10^{-4} M Al
- FI-85-8: 1.5×10^{-4} M Al
- FI-85-9: 1.0×10^{-4} M Al

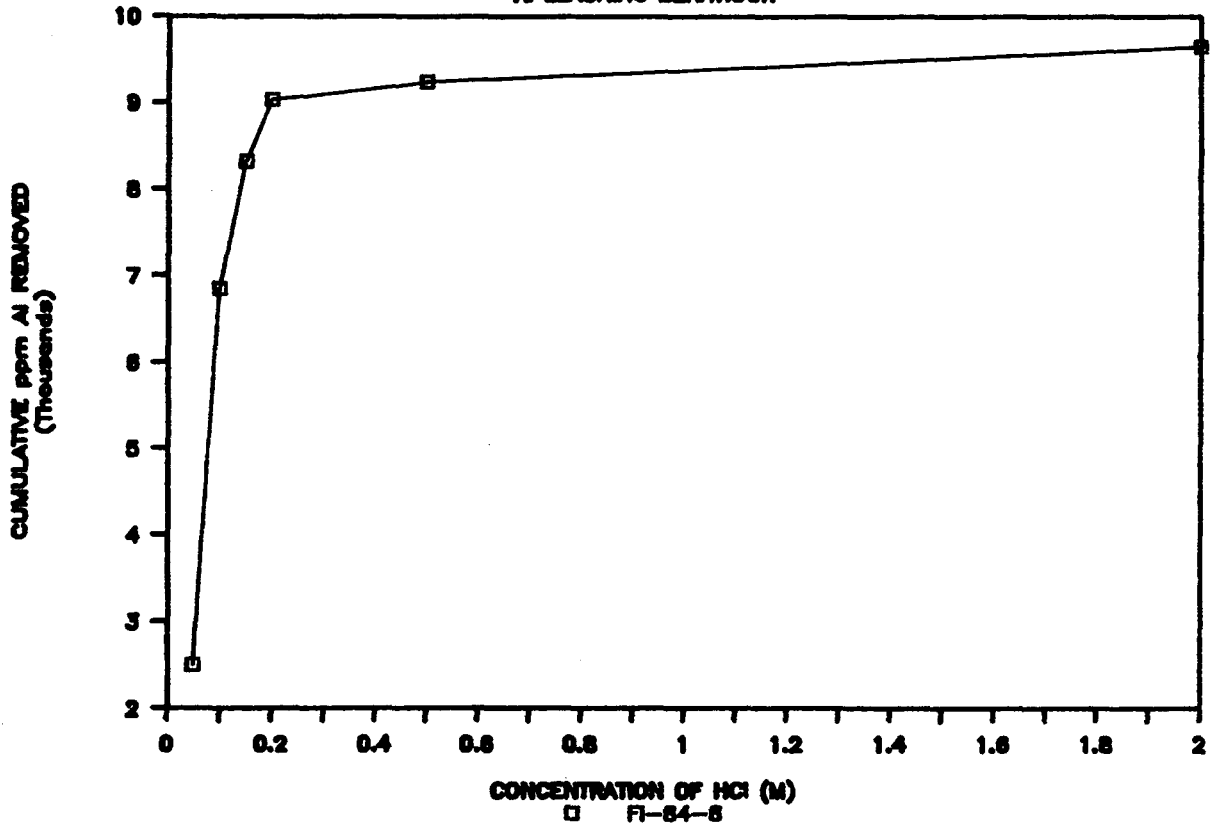
Figure 9. Cumulative removal of Al from silica deposits from geothermal brines at HGP-A as a function of HCl concentration.

- a. X-29-1: silica precipitated by addition of NaOH to spent brine, final pH $\gg 9.0$
- X-29-5: silica precipitated by addition of 2.5×10^{-4} M Al to unflashed brine at pH = 8.0

- b. X-29-2: silica deposited by natural precipitation in spent brine pH ~ 7.5
- X-29-3: silica scale deposit from turbine nozzle inlet.
- X-29-4: silica precipitated by addition of 2.5×10^{-4} M Fe(III) to unflashed brine at pH = 8.0

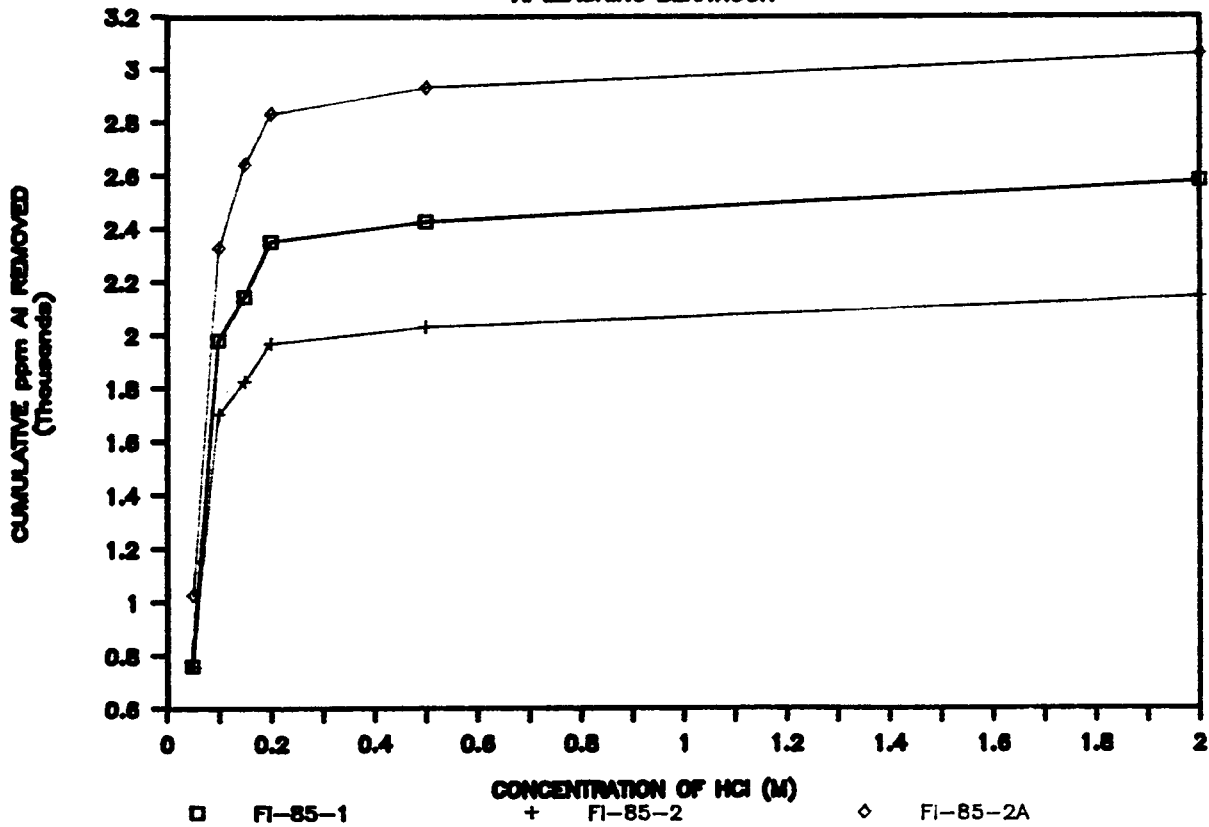
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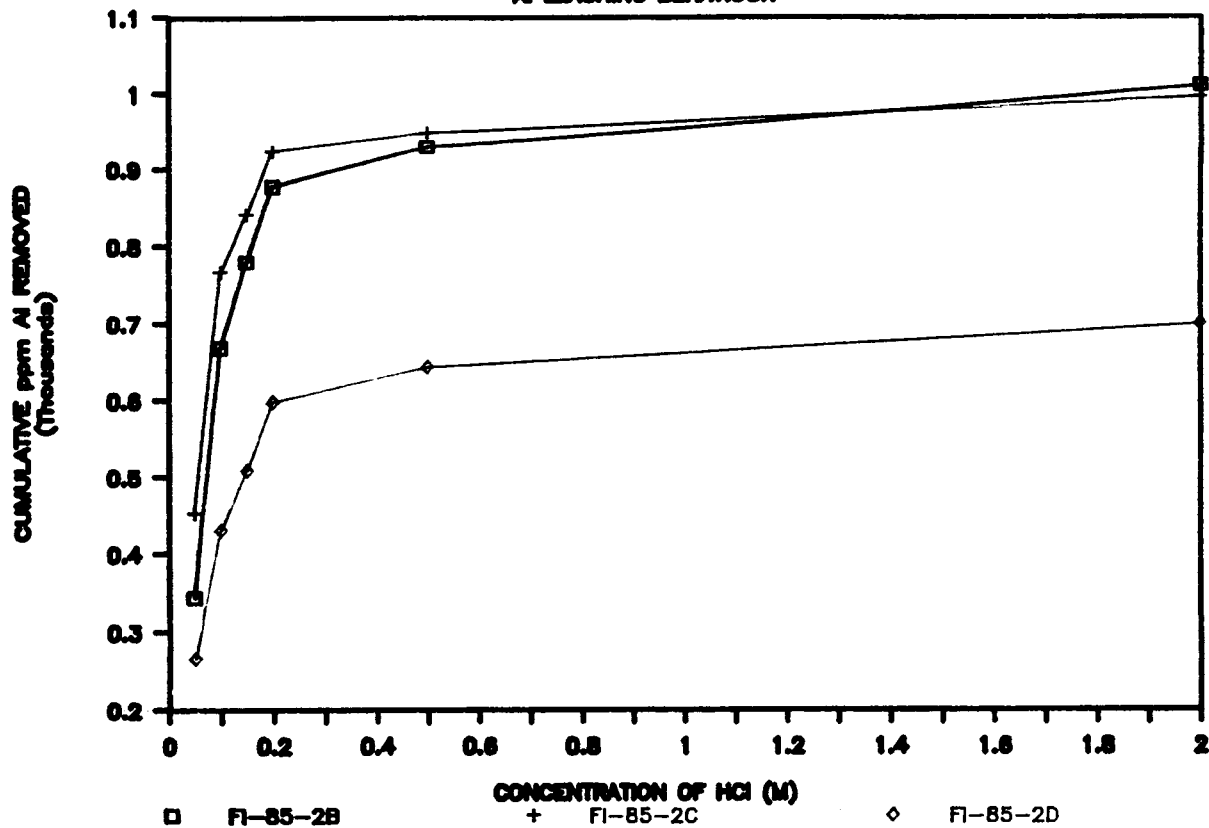
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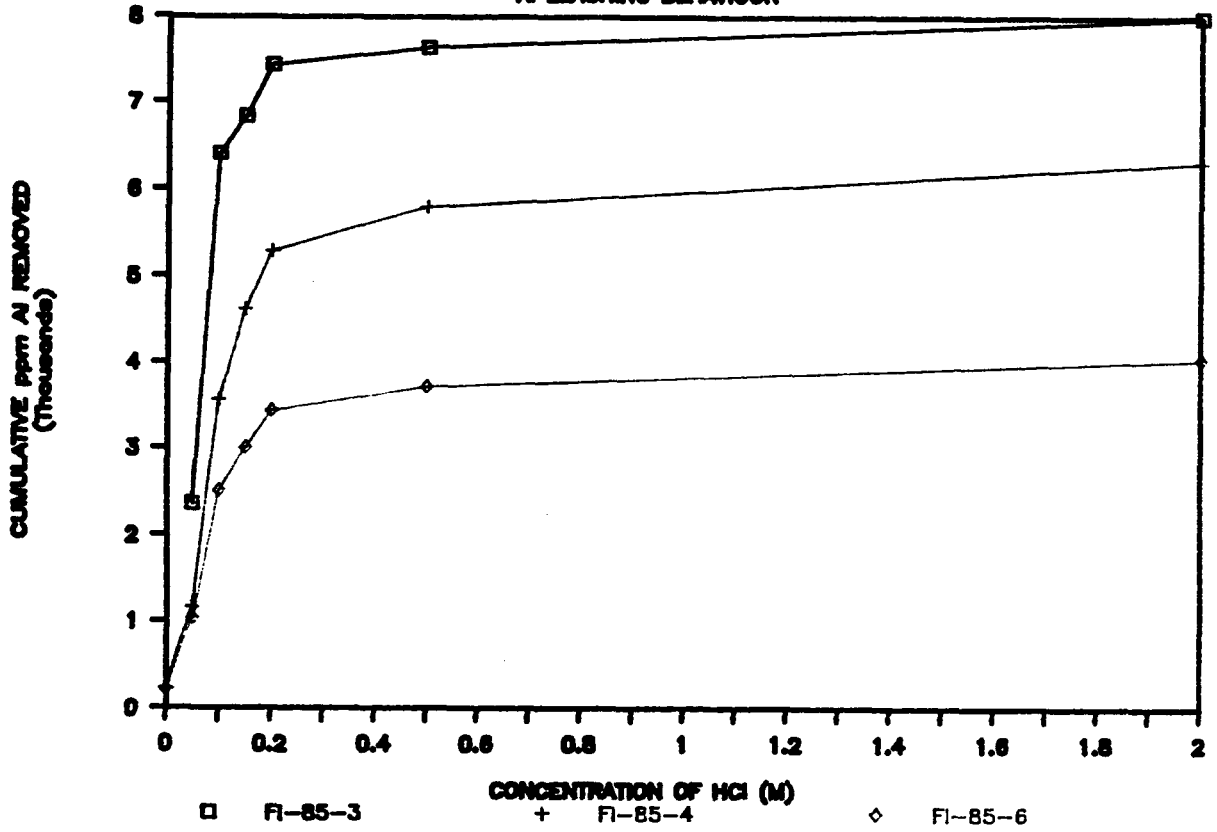
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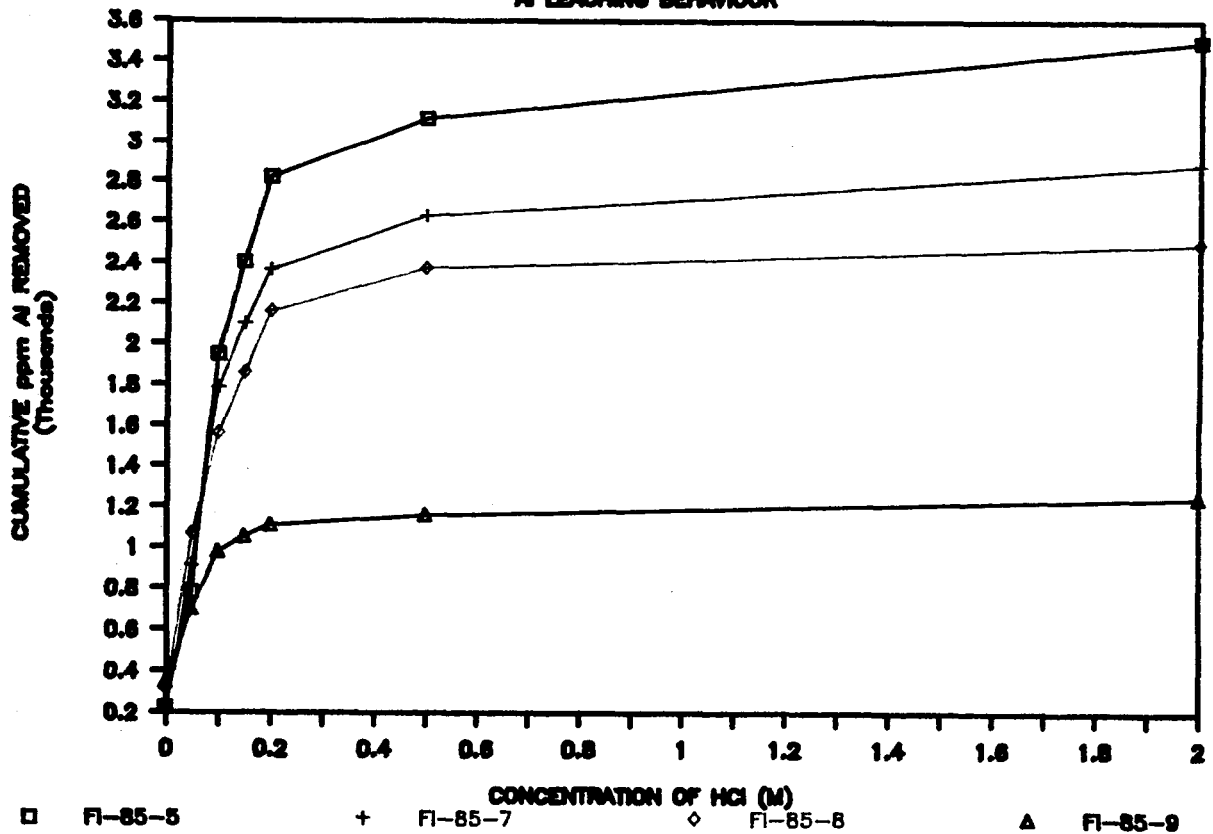
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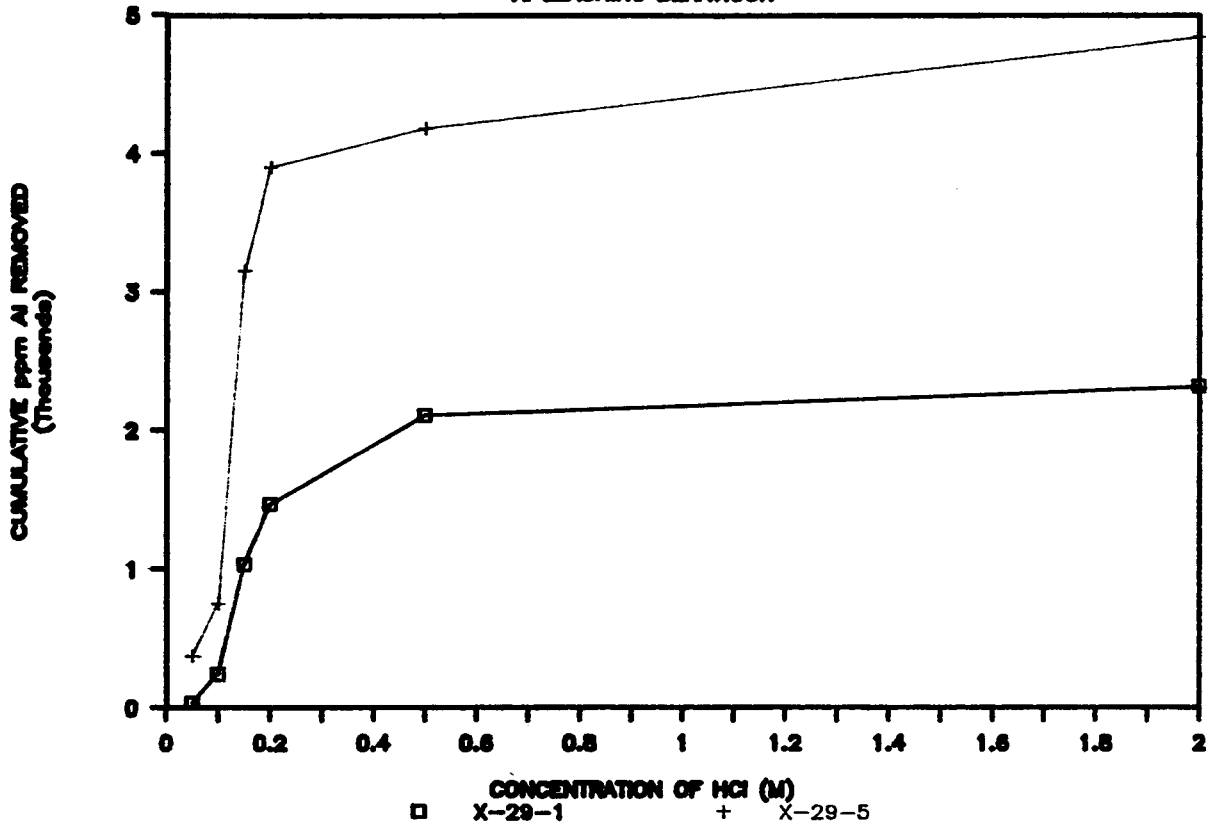
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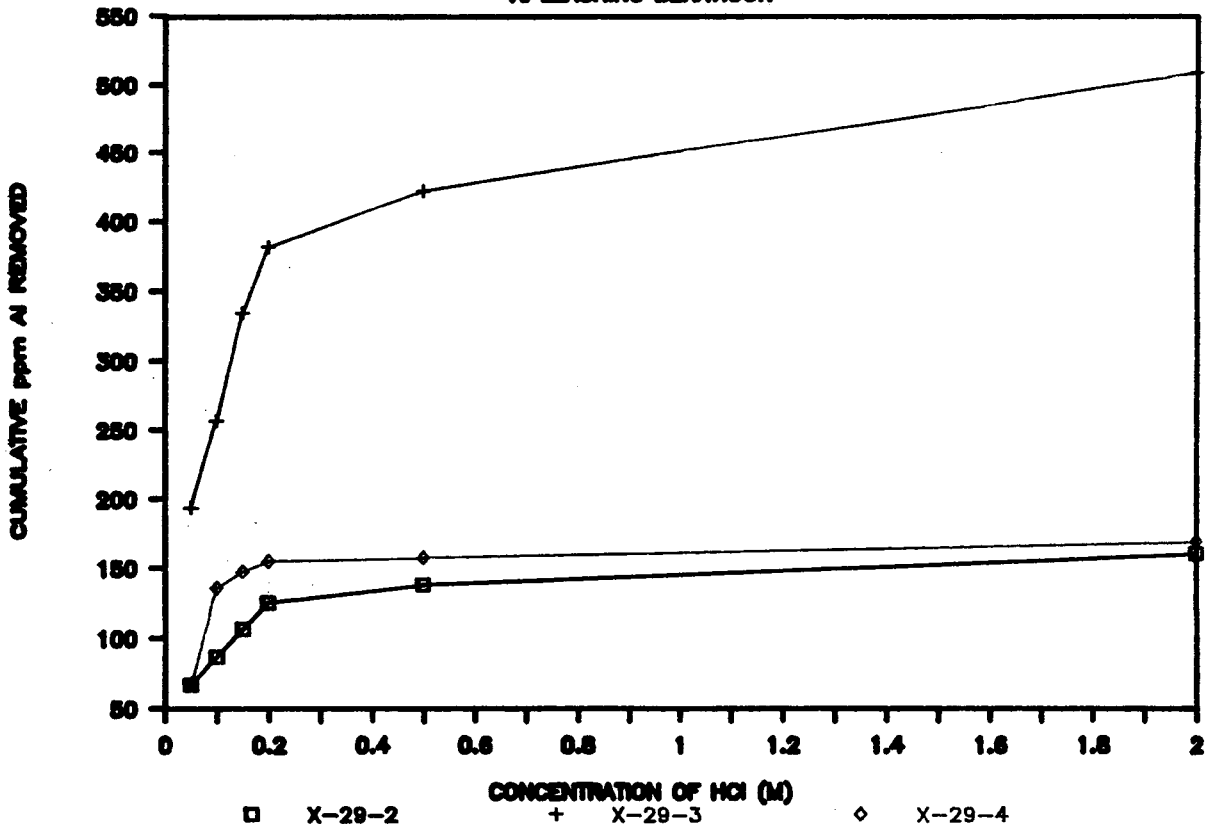
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Al LEACHING BEHAVIOUR



much lower Al concentrations probably resulting from incorporation of aqueous Al in the brine rather than from contamination in the iron sulfate flocculant. Direct incorporation of Al from the brine is supported by the data presented in Figure 9b. Sample X-29-3, which was previously described as a naturally precipitated scale, accumulated over a much longer period of time and was thus in extended contact with geothermal fluids allowing for a greater extent of Al scavenging by the silica. The significantly higher concentration of Al removed (near 500 ppm) from this sample during leaching with HCl is in agreement with this suggestion. Generally the small amount of Al present in the precipitates described above is more tightly bound to the silica and therefore much more difficult to remove. Data for sample X-29-2 in Figure 9b and for the samples in Figure 10 support this contention as the amount of silica removed increases significantly with higher concentrations of HCl used for leaching.

Iron :

Figure 11 depicts the cumulative removal of iron from samples prepared by the addition of ferric sulfate to flashed brine. Unlike the results for the samples precipitated by the addition of Al where most of the metal was removed by low concentrations of HCl independent of the amount of Al added (e.g. in Figures 6 and 7; note the generally asymptotic shape of curves), the removal curves for iron are significantly different from one another. They initially are asymptotic (samples which were precipitated in the presence of 1.5×10^{-4} M or less added Fe) but show increasingly greater removal of the metal from the samples precipitated in the presence of higher Fe concentrations upon leaching with HCl above 0.5 M. Such a trend would indicate that initially the Fe added causes enhanced precipitation of silica; a portion of the Fe is adsorbed on the surface of the silica and the rest is incorporated by cross-linking in the silica structure as suggested by De Carlo and Ronay (1986). Additions of Fe above 1.5×10^{-4} M result in actual incorporation of Fe in the silica structure, physical entrapment between particles of silica, as well as surface adsorption on the silica. The Fe which can be leached with greater than 0.5 M HCl may be of the entrapped variety whereas that removed by less than 0.5 M HCl is most likely present as surface adsorbed Fe hydroxy complexes held by electrostatic attractions or specific adsorption. The absolute amount of Fe leached from the silica precipitates generally varies in a linear manner with the amount of Fe used to precipitate the samples. There are, however, notable differences in the relative removal of Fe which become apparent when comparing the data from Table 1 and Figure 11. Sample FI-84-7 exhibits the least amount of Fe removal on a relative basis (i.e. nearly 71%) while sample 84-1 has the highest (i.e. 94%); relative removal increases generally with the concentration of Fe added as a flocculant. Such behaviour would seem to confirm that at lower concentrations proportionally more of the added Fe is bound (unavailable), whereas at higher concentrations it is easier to remove a large fraction of the total Fe. Another way to evaluate these data is in terms of the Fe concentration remaining in the silica after leaching. Simple calculations yield 1.22 mg/g Fe in FI-84-1, 1.91 mg/g in 84-2, 1.45 mg/g in 84-3, 1.94 mg/g in 84-4, 1.30 mg/g in 84-5, 1.29 mg/g in 84-6, and 1.05 mg/g in 84-7. The same general final Fe content of the silica after treatment (except for FI-84-2 and 84-4) would favor a mechanism limiting the Fe incorporation at bridging sites to a point where the silica structure has achieved a definite composition. Fe present above this concentration would be in labile sites such as at the electrical double layer of the silica surface or as chemisorbed surface hydroxy complexes. It is interesting to note that samples prepared in the initial phase of this research and leached in-situ also contained nearly identical final concentrations of Fe (see Figures 4 and 5) further supporting

TABLE 5

CUMULATIVE REMOVAL OF Fe FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.20	0.50	2.00
	Concentration of Fe (in ppm)						
FI-84-1B	84.20	2470.00	2030.00	5820.00	1880.00	4160.00	3900.00
cum.	84.20	2554.20	4584.20	10404.20	12284.20	16444.20	20344.20
original							21563.00
FI-84-2	11.80	441.00	979.00	1670.00	985.00	2120.00	4780.00
cum.	11.80	452.80	1431.80	3101.80	4086.80	6206.80	10986.80
original							12900.00
FI-84-3	6.40	579.00	1040.00	2030.00	1020.00	1520.00	2740.00
cum.	6.40	585.40	1625.40	3655.40	4675.40	6195.40	8935.40
original							10383.00
FI-84-4	5.30	647.00	942.00	2120.00	906.00	1120.00	1150.00
cum.	5.30	652.30	1594.30	3714.30	4620.30	5740.30	6890.30
original							8833.00
FI-84-5	8.20	1100.00	981.00	1950.00	701.00	810.00	901.00
cum.	8.20	1108.20	2089.20	4039.20	4740.20	5550.20	6451.20
original							7750.00
FI-84-6	6.80	817.00	766.00	1170.00	539.00	513.00	639.00
cum.	6.80	823.80	1589.80	2759.80	3298.80	3811.80	4450.80
original							5750.00
FI-84-7	5.90	1090.00	495.00	465.00	216.00	138.00	163.00
cum.	5.90	1095.90	1590.90	2055.90	2271.90	2409.90	2572.90
original							3623.00
FI-84-8		7.80	23.90	23.10	10.80	9.30	9.40
cum.		0.00	26.70	43.20	43.20	43.20	43.40
FI-85-1		4.90	5.80	2.70	2.40	1.40	4.20
cum.		41.60	52.50	56.30	58.00	58.50	60.50
FI-85-2		3.40	3.30	1.80	1.50	1.00	2.10
cum.		3.40	6.70	8.50	10.00	11.00	13.10
FI-85-2A		5.60	2.00	2.00	1.10	1.20	2.40
cum.		5.60	7.60	9.60	10.70	11.90	14.30
FI-85-2B		2.90	3.00	2.60	2.30	1.70	4.90
cum.		2.90	5.90	8.50	10.80	12.50	17.40
FI-85-2C		3.00	1.70	1.70	2.20	1.10	4.30
cum.		3.00	4.70	6.40	8.60	9.70	14.00
FI-85-2D		1.60	3.10	3.20	2.70	2.80	7.10
cum.		1.60	4.70	7.90	10.60	13.40	20.50

TABLE 5

CUMULATIVE REMOVAL OF Fe FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.20	0.50	2.00
	Concentration of Fe (in ppm)						
FI-85-3		3.60	5.90	4.60	2.80	3.00	7.80
cum.		3.60	9.50	14.10	16.90	19.90	27.70
FI-85-4	5.80	28.70	2.30	2.50	1.90	1.60	3.70
cum.	5.80	34.50	36.80	39.30	41.20	42.80	46.50
FI-85-5	1.50	1.80	3.20	2.80	2.70	2.60	4.50
cum.	1.50	3.30	6.50	9.30	12.00	14.60	19.10
FI-85-6	3.80	1.20	2.00	1.90	1.60	1.40	3.60
cum.	3.80	5.00	7.00	8.90	10.50	11.90	15.50
FI-85-7	0.10	0.80	2.20	1.50	1.30	1.20	2.20
cum.	0.10	0.90	3.10	4.60	5.90	7.10	9.30
FI-85-8	2.60	2.90	4.10	3.20	3.30	2.80	6.90
cum.	2.60	5.50	9.60	12.80	16.10	18.90	25.80
FI-85-9	3.30	0.30	2.10	2.40	4.10	3.60	2.90
cum.	3.30	3.60	5.70	8.10	12.20	15.80	18.70
FI-90-1		170.00	1090.00	697.00	258.00	65.20	104.00
cum.		170.00	1260.00	1957.00	2215.00	2280.20	2384.20
FI-93-1		461.00	841.00	1020.00	2790.00	994.00	1110.00
cum.		461.00	1302.00	2322.00	5112.00	6106.00	7216.00
FI-94-2		651.00	1140.00	1500.00	1940.00	1170.00	908.00
cum.		651.00	1791.00	3291.00	5231.00	6401.00	7309.00
FI-95-1		482.00	595.00	1380.00	1110.00	480.00	206.00
cum.		482.00	1077.00	2457.00	3567.00	4047.00	4253.00
X-29-1		4.20	1.40	2.10	1.60	10.60	8.00
cum.		4.20	5.60	7.70	9.30	19.90	27.90
X-29-2		91.30	33.50	26.70	25.50	4.90	24.30
cum.		91.30	124.80	151.50	177.00	181.90	206.20
X-29-3		733.00	203.00	429.00	199.00	114.00	530.00
cum.		733.00	936.00	1365.00	1564.00	1678.00	2208.00
X-29-4		996.00	10100.00	4530.00	1460.00	798.00	889.00
cum.		996.00	11096.00	15626.00	17086.00	17884.00	18773.00
X-29-5		1.50	10.10	25.50	8.40	4.20	6.00
cum.		1.50	11.60	37.10	45.50	49.70	55.70

Figure 10. Removal of Al from silica precipitated by addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

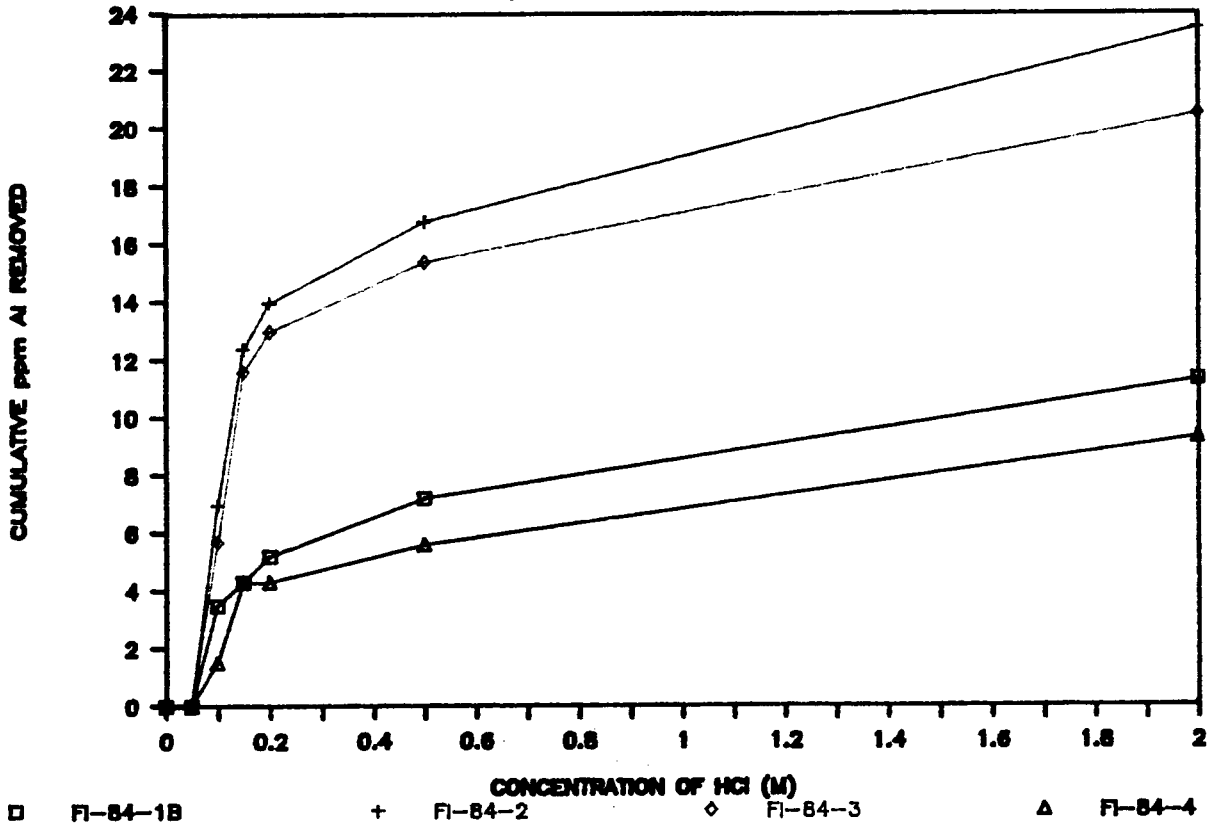
- a. FI-84-1B: 5.0×10^{-4} M Fe(III)
FI-84-2: 4.0×10^{-4} M Fe(III)
FI-84-3: 3.0×10^{-4} M Fe(III)
FI-84-4: 2.5×10^{-4} M Fe(III)
- b. FI-84-5: 2.0×10^{-4} M Fe(III)
FI-84-6: 1.5×10^{-4} M Fe(III)
FI-84-7: 1.0×10^{-4} M Fe(III)

Figure 11. Removal of Fe from silica prepared by the addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

- a. FI-84-1B: 5.0×10^{-4} M Fe(III)
FI-84-2: 4.0×10^{-4} M Fe(III)
FI-84-3: 3.0×10^{-4} M Fe(III)
FI-84-4: 2.5×10^{-4} M Fe(III)
- b. FI-84-5: 2.0×10^{-4} M Fe(III)
FI-84-6: 1.5×10^{-4} M Fe(III)
FI-84-7: 1.0×10^{-4} M Fe(III)

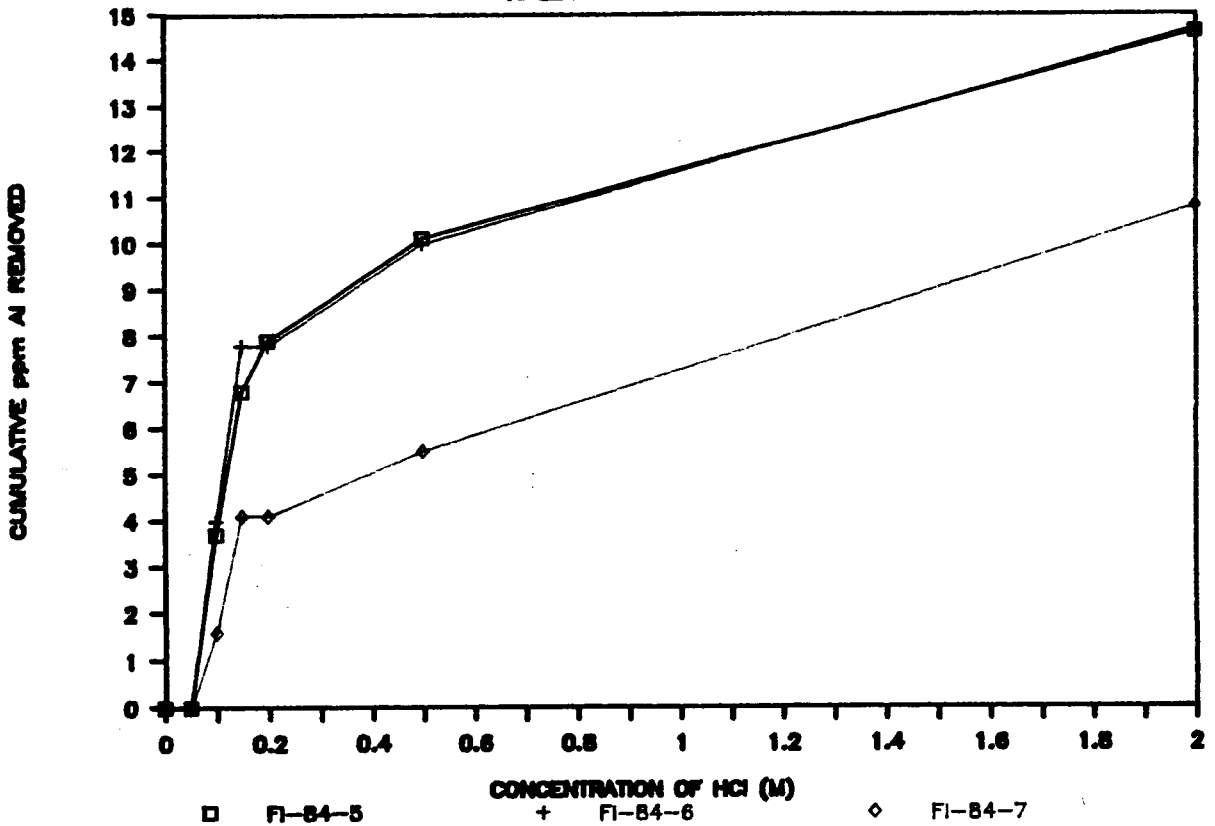
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Al LEACHING BEHAVIOUR



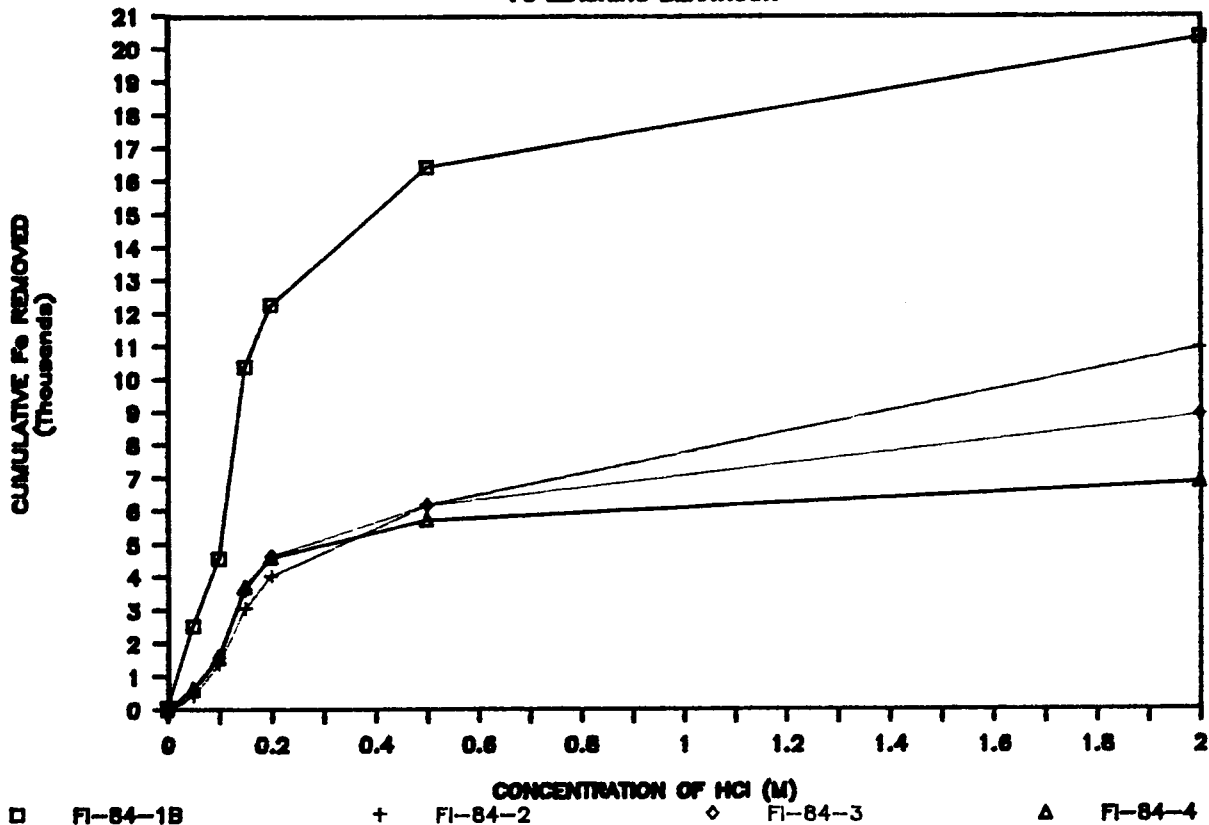
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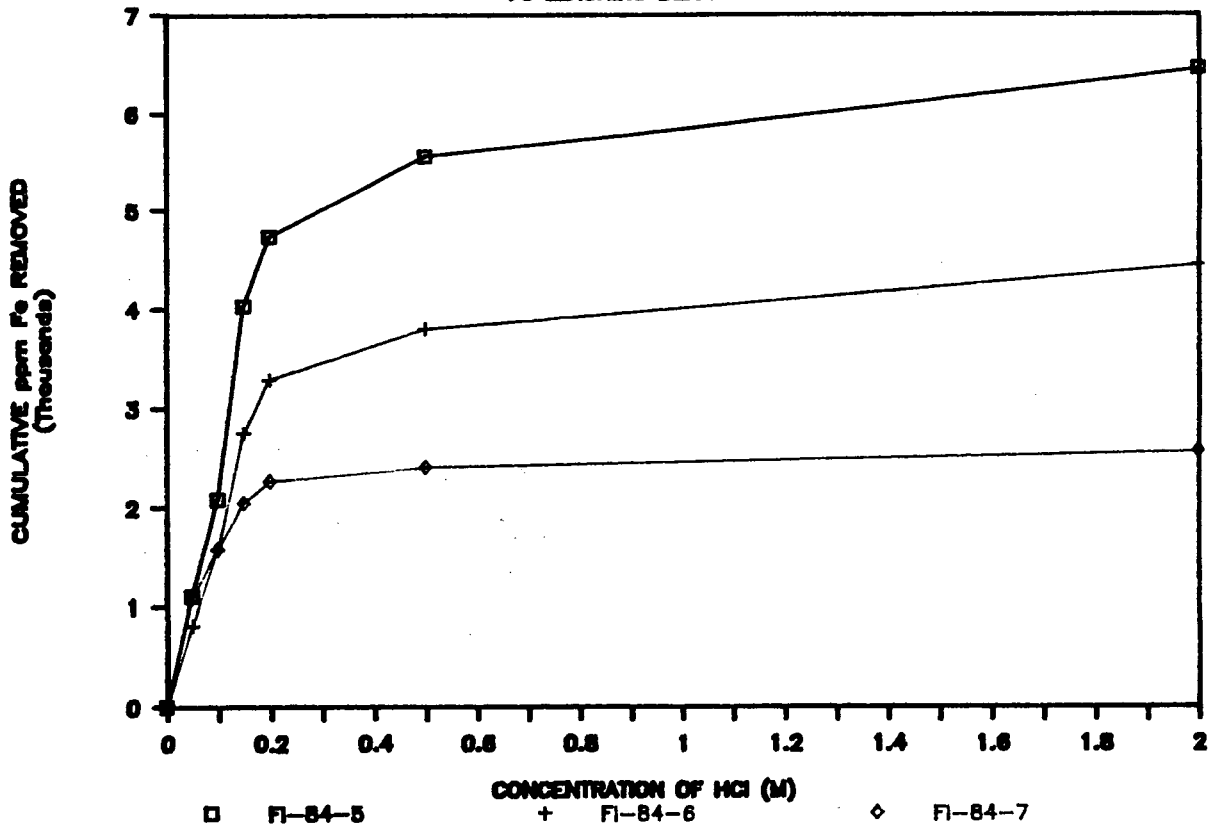
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Fe LEACHING BEHAVIOUR



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Fe LEACHING BEHAVIOUR



the proposed hypothesis. The amount of Fe which remained after leaching of the samples treated at HGP-A (<0.2 mg/g) is considerably lower than that in samples leached at HIG; this behaviour may indicate that the silica ages with time possibly resulting in metal species which are more tightly bound. We discuss this further in the Ca section. In order to better understand the nature of Fe-Si interactions further work under controlled kinetic conditions as well as spectroscopic investigations of the bonding between elements in silica are needed. Studies under conditions permitting reproducible kinetics are particularly needed. In this work there were instances in which samples prepared under different conditions were left in contact with the brine for unequal periods of time. This can affect the amount of free Fe incorporated from the bulk solution (particularly by scavenging), and lead to silica scale of different properties. Since silica is such an efficient scavenger, the experiments are particularly prone to problems of this nature.

The hypothesis proposed above appears consistent with data from samples FI-90-1 and FI-95-1. The removal curves for the two samples are shown in Figure 12a and exhibit nearly a factor of two difference in the amount of Fe leached although both samples were prepared similarly and had concentrations of 4.46 mg/g and 5.22 mg/g Fe respectively in the solid prior to leaching with acid. The difference in removal may arise from the fact that sample FI-95-1 was precipitated with laurylammonium chloride (a cationic surfactant) present. The negatively charged surface of hydroxy complexes of Fe in the pH range of the silica preparation experiments will cause adsorption of the positively charged laurylammonium ion and may prevent some of the Fe from being available for bridging in the silica. In such a case attack by HCl will cause separation of the surfactant ion from the Fe hydroxy complexes due to acid dissolution at low pH and the development of a positive surface charge on Fe complexes at low pH thus precluding electrostatic attractions between the two entities. This results in a larger fraction of labile Fe in the sample prepared in the presence of surfactant. The amount of Fe remaining in the two silica samples after leaching is calculated by difference to be 2.27 mg/g and 0.97 mg/g respectively. The former is higher than the upper end of the range of concentrations present in samples FI-84-1 to 84-7, the latter is near the lower end of the range found in that series. From these observations it is speculative to ascertain the nature of the labile versus bound Fe in these two samples. It is also probable that kinetics, over which we had little control during the course of precipitation/leaching experiments, may play an important role. Such kinetic control on the metal content of silica scale has been previously noted (Thomas, pers. comm. 1986).

Samples which were formed by slow precipitation under natural conditions or by enhanced flocculation with aluminum salts exhibit increased removal of Fe as a function of the acid concentration of the leach solution. The data are presented in Figures 13 and 14. In figure 13a the high concentration of Fe removed from the turbine nozzle inlet scale sample indicates that a large quantity of Fe had accumulated in the silica as a result of scavenging from geothermal fluids over an extended period of time. Comparing the data from Table 2 to that presented in Figure 13a reveals that although nearly 2.2 mg/g Fe has been removed by successive leachings, this amount only represents about 20% of that initially present in the scale. It would appear that the rest of the Fe is tightly bound in the silica structure. This is not surprising as slow precipitation of this sample would have favored the incorporation of Fe in structural sites as opposed to simple surface adsorption or entrapment within the deposit. Similarly shaped removal curves are apparent in Figure 14 where the small amount of Fe present (probably from incorporation of dissolved Fe in the brine) is increasingly removed as a function of acid concentration. Sample X-29-4 which was precipitated by the addition of ferric sulfate to unflushed brine exhibits a removal curve reminiscent of those for samples

Figure 12. Removal of Fe from silica prepared by the addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

- a. FI-90-1: 1.25×10^{-4} M Fe(III), and rinsed with distilled deionized (d.d.)
 FI-93-1: 2.5×10^{-4} M Fe(III), not rinsed FI-94-2: 2.5×10^{-4} M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant
 FI-95-1: 1.5×10^{-4} M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant, and rinsed with d.d. H_2O
- b. X-29-1: silica precipitated by addition of NaOH to spent brine pH ≥ 9.0
 X-29-2: silica deposited by natural precipitation in spent brine pH ~ 7.5
 X-29-5: silica prepared by addition of 2.5×10^{-4} M Al to unflashed brine

Figure 13. Cumulative removal of Fe from silica precipitates as a function of HCl concentration.

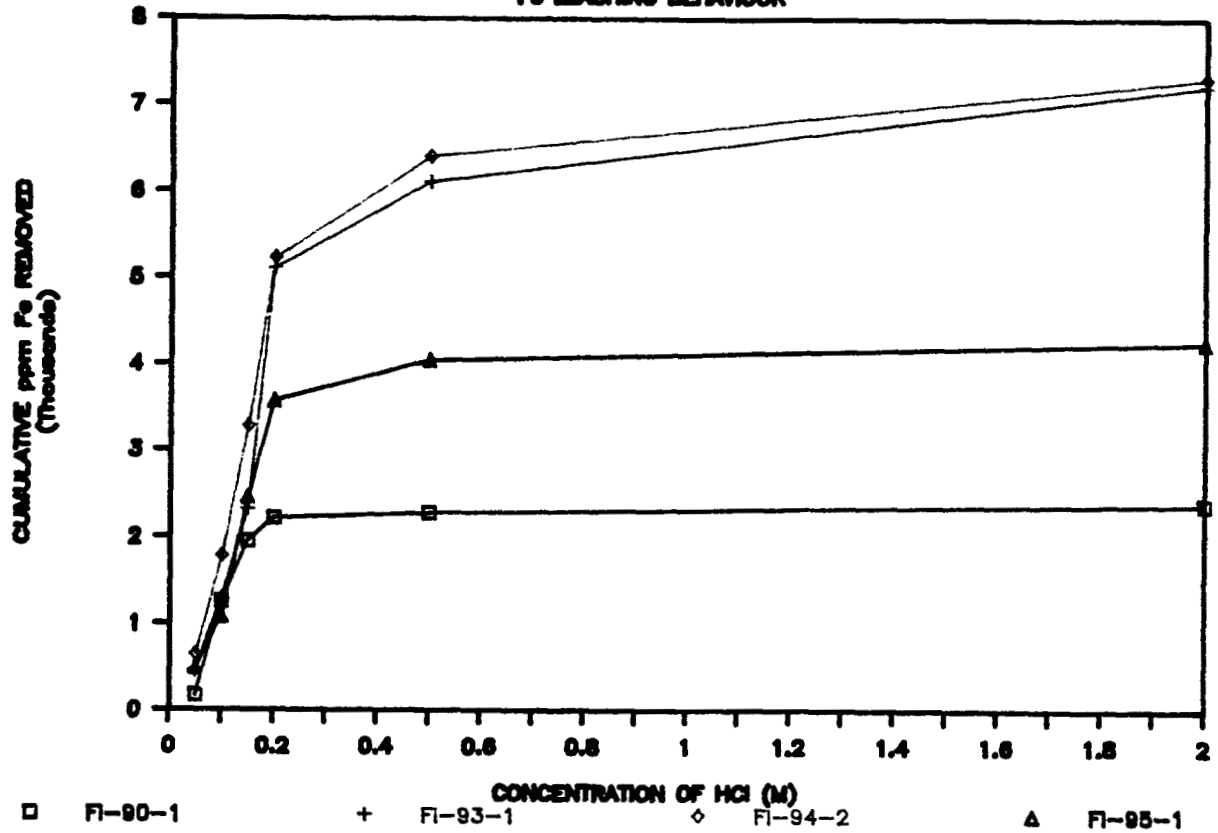
- a. X-29-3: silica deposits by natural precipitation at the turbine nozzle inlet
- b. X-29-4: silica precipitated by the addition of 2.5×10^{-4} M Fe(III) as ferric sulfate to unflashed brine

Figure 14. Cumulative removal of Fe from silica precipitated by the addition of $\text{Al}_2(\text{SO}_4)_3$ as a function of HCl concentration.

- a. FI-85-3: 5.0×10^{-4} M Al
 FI-85-4: 4.0×10^{-4} M Al
 FI-85-8: 1.5×10^{-4} M Al
 FI-85-9: 1.0×10^{-4} M Al
- b. FI-85-5: 3.0×10^{-4} M Al
 FI-85-6: 2.5×10^{-4} M Al
 FI-85-2: 2.0×10^{-4} M Al

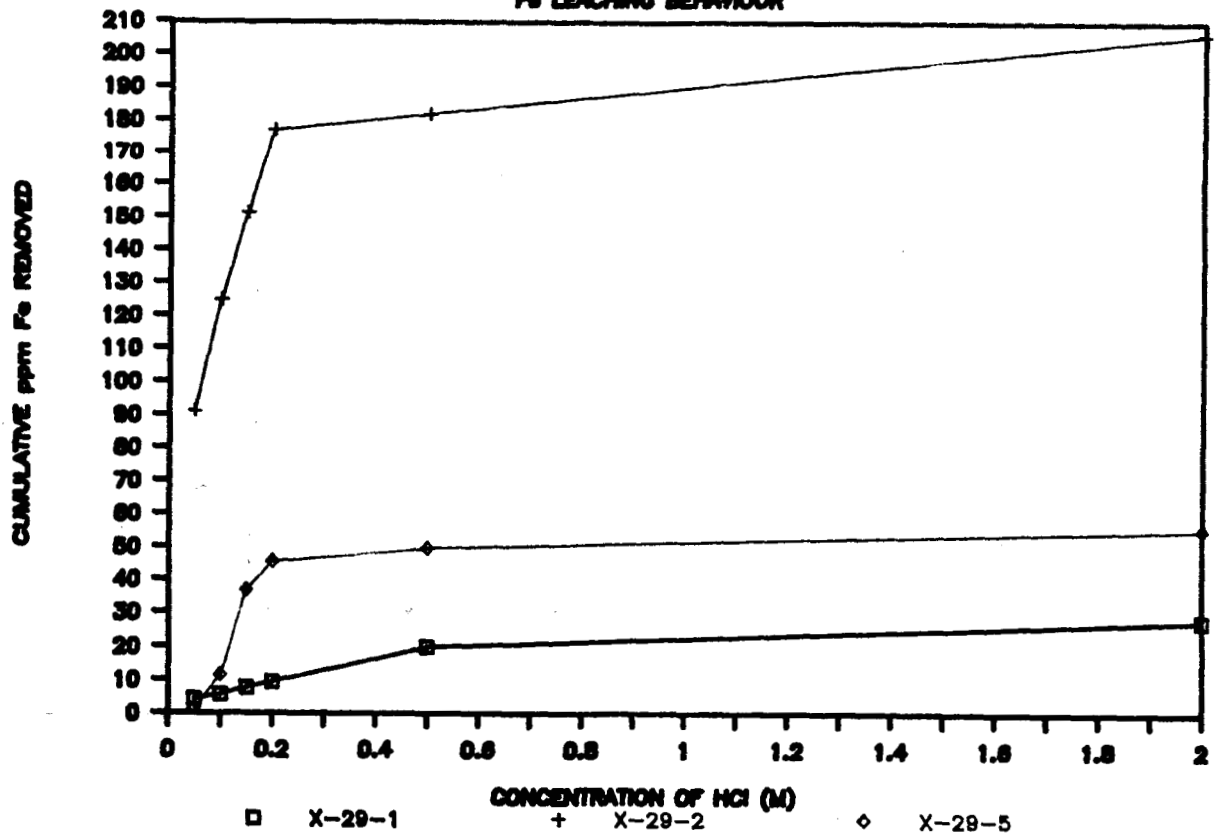
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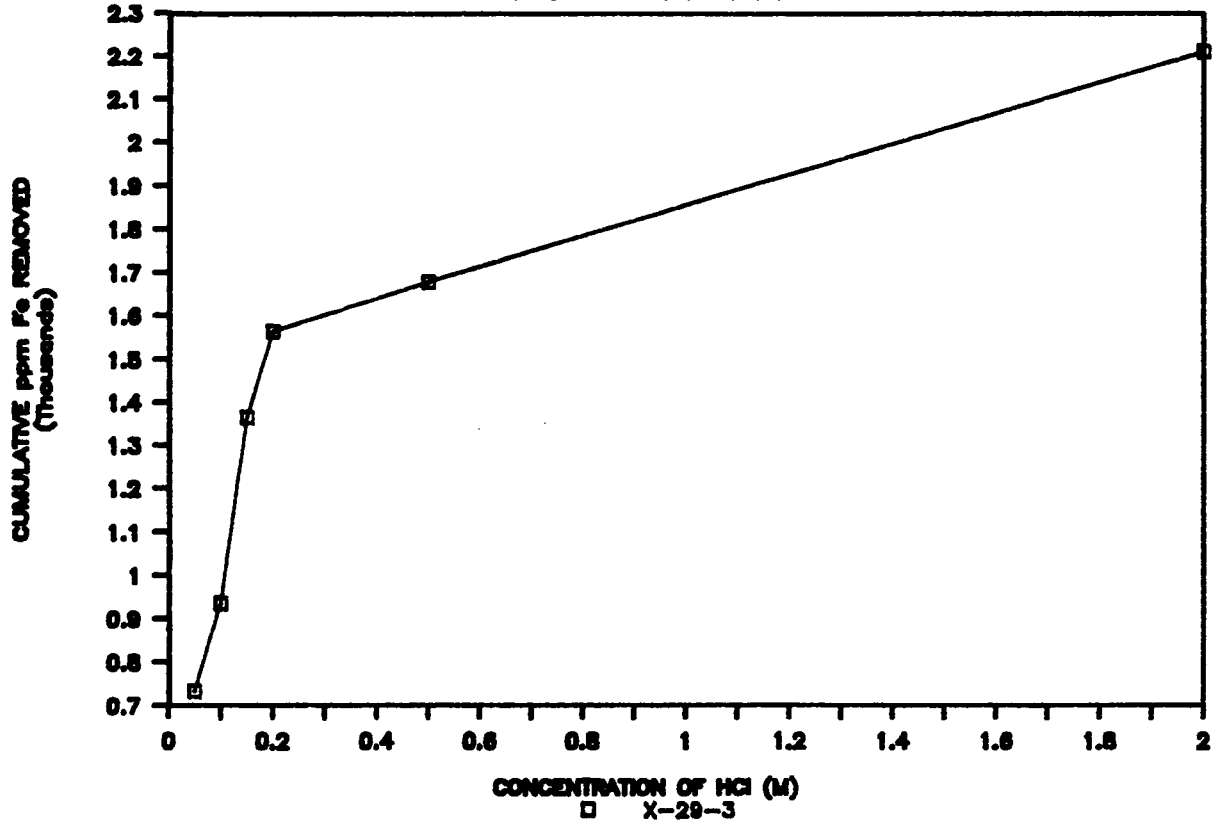
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Fe LEACHING BEHAVIOUR



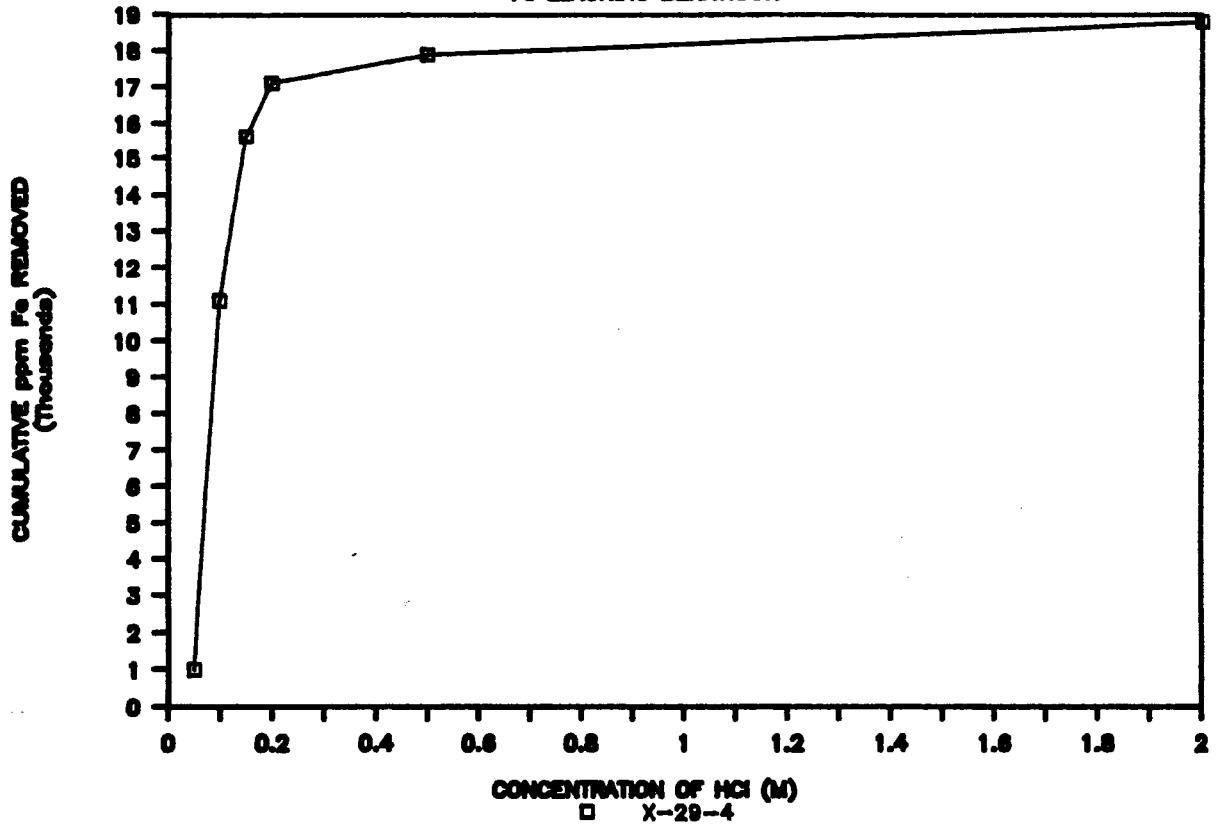
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Fe LEACHING BEHAVIOUR



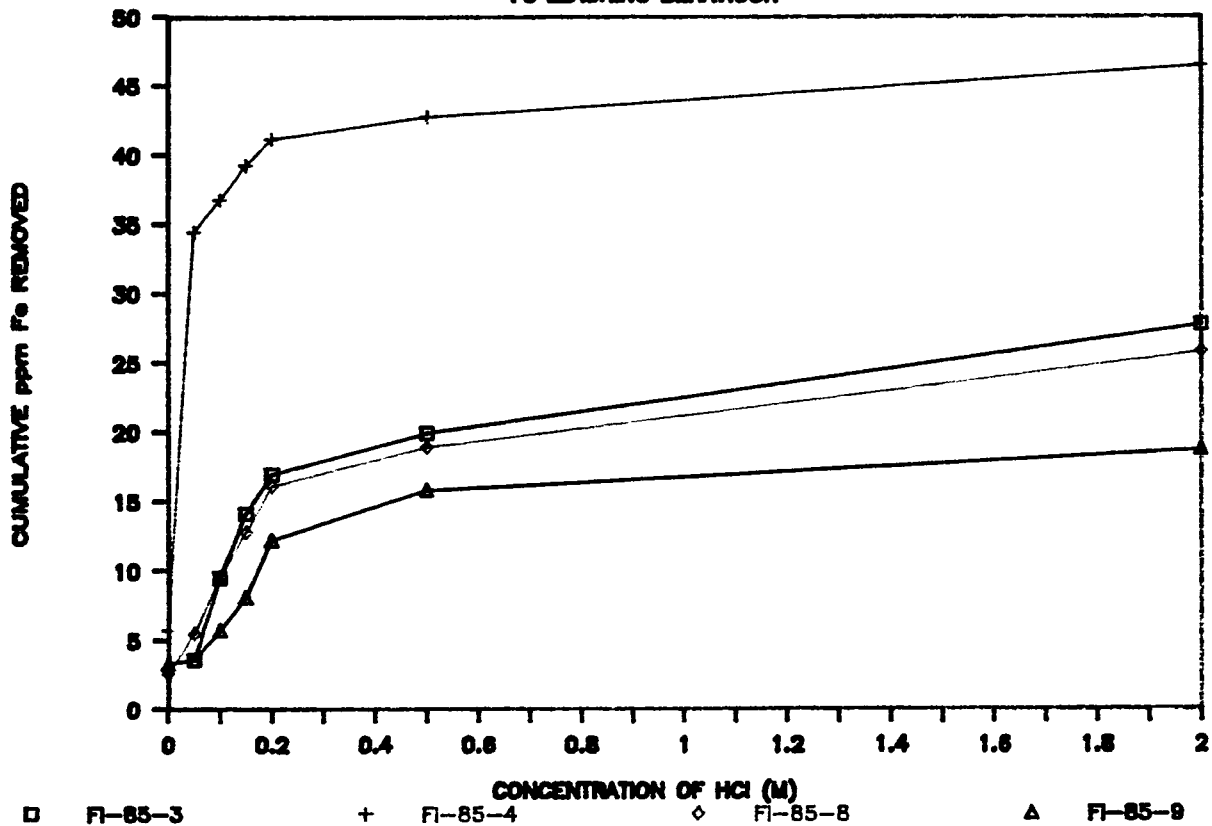
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Fe LEACHING BEHAVIOUR



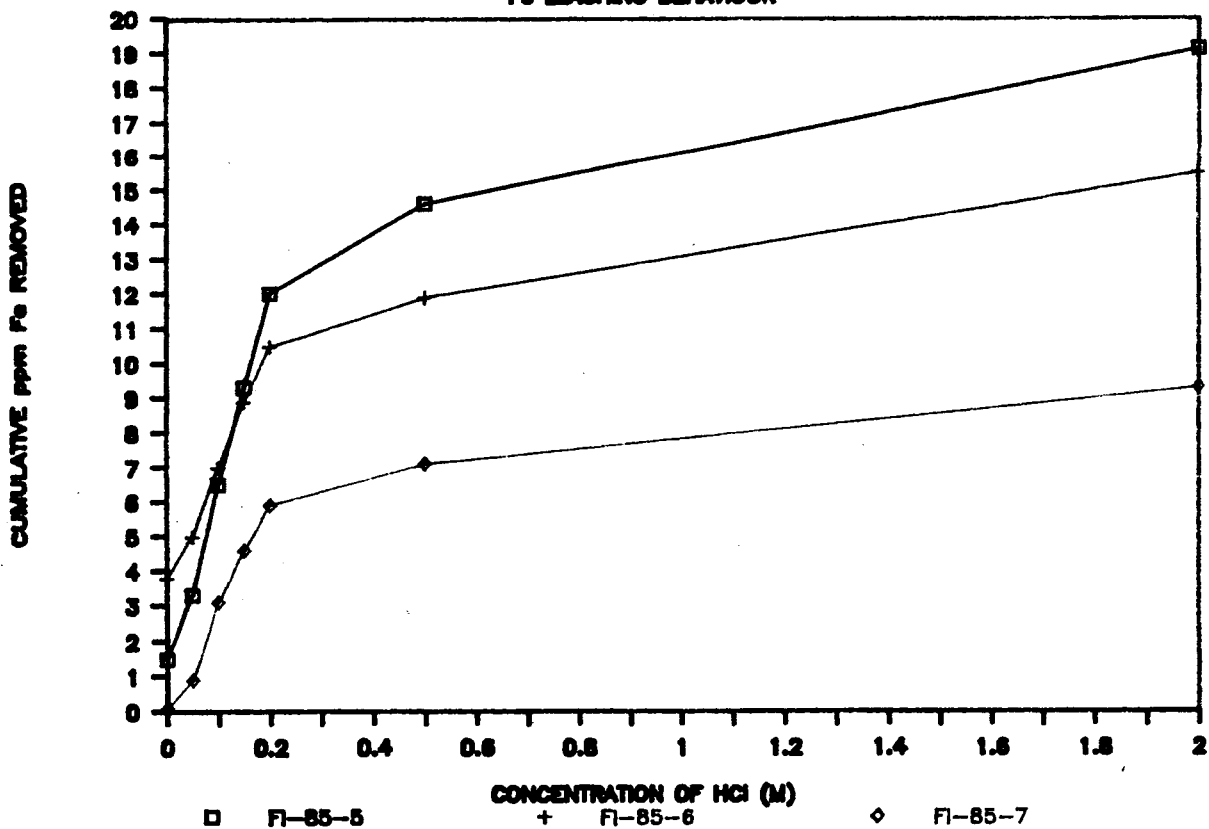
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Fe LEACHING BEHAVIOUR



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Fe LEACHING BEHAVIOUR



prepared by addition of low concentrations of Fe to flashed brine. The asymptotic nature of the curve indicates that the Fe removed is quite labile and probably not bound in structural bridging sites. Again the kinetics of the precipitation process must play an important role in governing the nature of the Fe in this sample.

Potassium:

Removal curves for K from silica prepared by enhanced flocculation are shown in Figures 15 through 19. From the shape of the curves it is readily apparent that the K in the samples is quite loosely bound to the silica. It appears that K is present as a result of entrapment of geothermal fluids in the silica and is thus easily leached from the precipitates. By the time the samples have been treated with 0.20 M HCl over 90% of the cumulative K removed has been leached out. A particularly notable feature of the removal curves is observable in Figure 15 which presents data for samples formed by addition of ferric sulfate to spent brine. Here we can observe that extremely little K is leached using 0.05 M HCl; most of the removal occurs with the 0.10 M through 0.20 M acid solutions. This apparently aberrant behaviour may be caused by a particularly poor contact between the 0.05 M HCl leach solution and the silica. Since all samples were treated simultaneously, it is possible that manual agitation of this particular run was inadequate to allow for a complete removal of otherwise available K. The situation was apparently remedied to by the 0.10 M step. This explanation may not be appropriate as the behaviour exhibited is not particular only to the samples prepared with ferric sulfate; examination of Figures 16, 17, 18, and 19a also reveals that very little K is removed when employing HCl which is more dilute than 0.10 M. In light of this fact, we would suggest that K, unlike Na, may have a specific attraction for the silica matrix or form surface complexes which require a low pH to desorb the K.

Observation of Figure 19b in which we present the leaching behaviour of naturally precipitated silica indicates that the K in samples X-29-2 and 29-3 although much less abundant (tens of ppm versus hundreds to thousands of ppm for enhanced precipitation silica), is tightly bound and is most likely involved in bonding with the silica. This is particularly evident with sample X-29-3 (turbine nozzle inlet deposit) which accumulated over long periods of time and thus had the opportunity to more effectively scavenge and bind the K.

Sodium:

Plots of the cumulative removal of Na as a function of HCl concentration are presented in Figures 20 through 25. As expected all samples except those which were formed by natural precipitation over extended time periods (X-29-2 and 29-3, shown in Figure 25b) exhibit removal patterns indicative of weakly bound and/or entrapped Na present due to its high abundance in the brine. All the Na is removed by water or very dilute HCl. In the cases where the data in Table 7 do not agree with those in Table 1 we attribute the difference to both analytical error and to a dilutionary effect on Na by water absorbed during the weighing of very small splits of the 110 degree C dried silica samples. These data compare very well with those presented in Table 1 for samples which were rinsed immediately after precipitation of the silica; in such samples (FI-90-1 through 95-1) the concentration of Na in the solids prior to leaching treatments is one to two orders of magnitude less than in silica which was not rinsed after collection. Even in these samples all the Na which remained in the samples prior to the leachings is removed by the first two HCl solutions of 0.05 M and 0.10 M. The very large quantity of Na entrapped or adsorbed by the silica during precipitation when inorganic flocculating agents are

TABLE 6

CUMULATIVE REMOVAL OF K FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.20	0.50	2.00
	Concentration of K (in ppm)						
FI-84-1B	155.560	11.110	172.222	36.806	65.972	31.944	47.917
cum.	155.560	166.670	338.892	375.698	441.670	473.614	521.531
FI-84-2	250.500	11.000	272.625	35.750	78.125	30.625	52.875
cum.	250.500	261.500	534.125	569.875	648.000	678.625	731.500
FI-84-3	246.310	9.360	298.276	38.300	86.946	31.404	25.355
cum.	246.310	255.670	553.946	592.246	679.192	710.596	735.951
FI-84-4	266.500	7.500	292.375	38.000	82.500	26.625	14.625
cum.	266.500	274.000	566.375	604.375	686.875	713.500	728.125
FI-84-5	209.260	8.330	158.102	31.481	96.759	34.954	58.796
cum.	209.260	217.590	375.692	407.173	503.932	538.886	597.682
FI-84-6	200.840	8.400	153.151	33.403	86.975	30.252	53.151
cum.	200.840	209.240	362.391	395.794	482.769	513.021	566.172
FI-84-7	253.400	8.740	93.204	22.330	66.019	25.971	47.816
cum.	253.400	262.140	355.344	377.674	443.693	469.664	517.480
FI-84-8		77.550	1931.818	561.224	163.435	38.605	40.455
cum.		77.550	2009.368	2570.592	2734.027	2772.632	2813.087
FI-85-1		354.290	1142.857	442.000	21.976	5.310	42.262
cum.		354.290	1497.147	1939.147	1939.147	1944.457	2008.695
FI-85-2		324.650	1327.907	162.802	91.047	40.116	26.512
cum.		324.650	1652.557	1815.359	1815.359	1855.475	1973.034
FI-85-2A		294.710	112.335	270.815	84.031	57.930	36.454
cum.		294.710	407.045	677.860	761.891	819.821	856.275
FI-85-2B		289.500	924.658	225.685	128.995	47.603	31.621
cum.		289.500	1214.158	1439.843	1568.838	1616.441	1648.062
FI-85-2C		329.950	824.879	128.623	134.179	33.575	23.792
cum.		329.950	1154.829	1283.452	1417.631	1451.206	1474.998
FI-85-2D		226.170	76.168	167.173	214.364	42.523	32.827
cum.		226.170	302.338	469.511	683.875	726.398	759.225
FI-85-3		290.240	1585.366	143.293	63.211	16.870	15.041
cum.		290.240	1875.606	2018.899	2018.899	2035.769	2114.021
FI-85-4		30.830	1225.296	435.771	146.640	51.186	24.605
cum.		30.830	1256.126	1691.897	1838.537	1889.723	1914.328

TABLE 6

CUMULATIVE REMOVAL OF K FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.20	0.50	2.00
	Concentration of K (in ppm)						
FI-85-5	337.010	25.200	787.402	298.819	142.421	74.311	45.866
cum.	337.010	362.210	1149.612	1448.431	1590.852	1665.163	1711.029
FI-85-6	249.030	24.900	918.290	241.926	108.755	40.272	24.125
cum.	249.030	273.930	1192.220	1434.146	1542.901	1583.173	1607.298
FI-85-7	284.100	25.100	647.490	205.649	97.908	68.305	72.259
cum.	284.100	309.200	956.690	1162.339	1260.247	1328.552	1400.811
FI-85-8	272.110	21.090	345.918	111.905	108.163	39.626	29.592
cum.	272.110	293.200	639.118	751.023	859.186	898.812	928.404
FI-85-9	317.650	15.690	387.909	46.405	44.608	22.222	25.000
cum.	317.650	333.340	721.249	767.654	812.262	834.484	859.484
FI-90-1		9.000	45.890	9.932	16.895	2.854	8.219
cum.		9.000	54.890	64.822	64.822	67.676	92.790
FI-93-1		12.080	252.053	48.551	81.159	8.333	17.874
cum.		12.080	264.133	312.684	312.684	321.017	420.050
FI-94-2		27.890	372.105	56.316	106.974	12.368	24.474
cum.		27.890	399.995	456.311	456.311	468.679	600.127
FI-95-1		19.230	369.952	50.481	137.019	15.385	35.096
cum.		19.230	389.182	439.663	576.682	592.067	627.163
X-29-1		4.480	575.871	2898.010	823.383	422.886	58.209
cum.		4.480	580.351	3478.361	4301.744	4724.630	4782.839
X-29-2			4.750	4.750	5.625	3.375	12.625
cum.			4.750	9.500	15.125	18.500	31.125
X-29-3			8.625	7.375	7.000	20.000	9.500
cum.			8.625	16.000	23.000	43.000	52.500
X-29-4		34.290	258.929	85.179	56.071	29.464	2.125
cum.		34.290	293.219	378.398	434.469	463.933	466.058
X-29-5		0.770	1650.485	1201.456	282.524	244.782	197.816
cum.		0.770	1651.255	2852.711	3135.235	3380.017	3577.833

Figure 15. Cumulative removal of K from silica prepared by the addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

- a. FI-84-1: 5.0×10^{-4} M Fe(III)
- FI-84-5: 2.0×10^{-4} M Fe(III)
- FI-84-6: 1.5×10^{-4} M Fe(III)
- FI-84-7: 1.0×10^{-4} M Fe(III)
- b. FI-84-2: 4.0×10^{-4} M Fe(III)
- FI-84-3: 3.0×10^{-4} M Fe(III)
- FI-84-4: 2.5×10^{-4} M Fe(III)

Figure 16. Cumulative removal of K from silica prepared by the addition of $\text{KAl}(\text{SO}_4)_2$ as a function of HCl concentration.

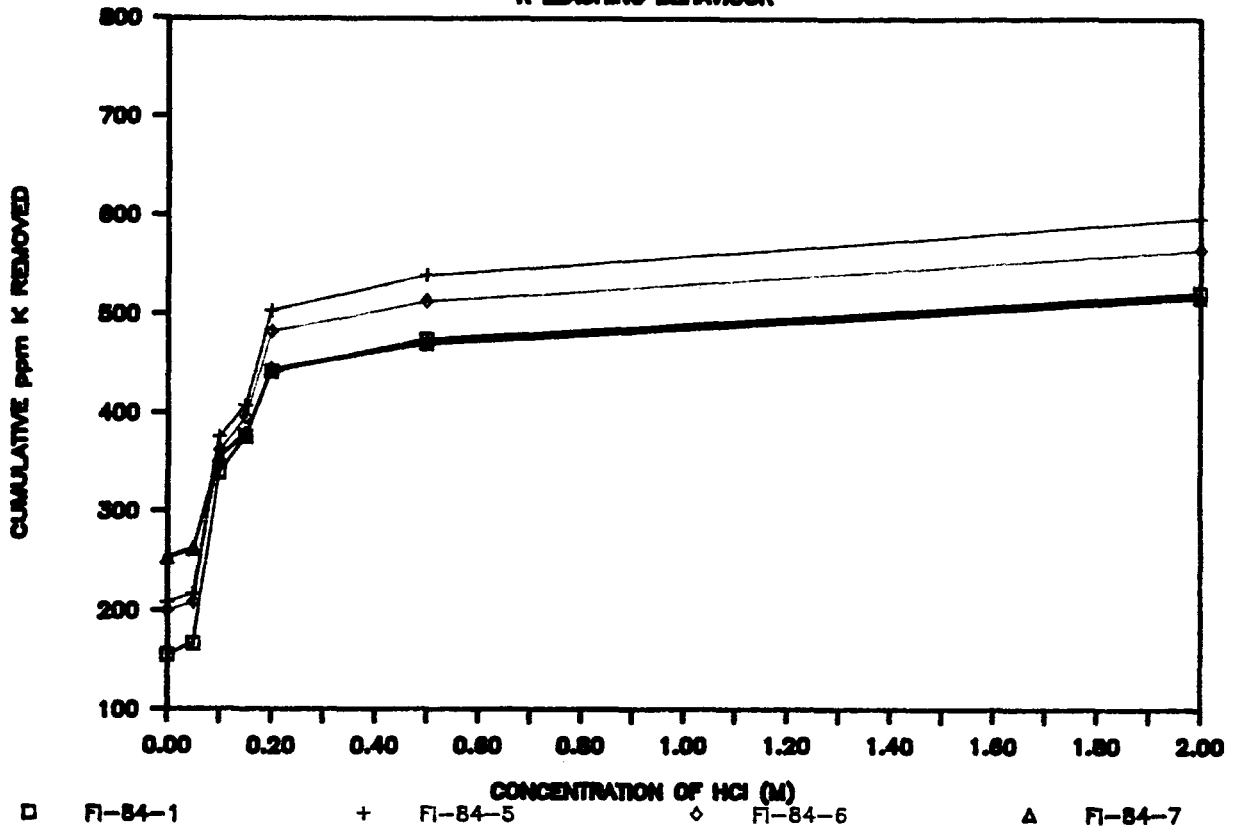
- a. FI-84-8: 5.0×10^{-4} M Al
- FI-85-1: 4.0×10^{-4} M Al
- FI-85-2: 3.0×10^{-4} M Al
- FI-85-2B: 2.0×10^{-4} M Al
- b. FI-85-2A: 2.5×10^{-4} M Al
- FI-85-2C: 1.5×10^{-4} M Al
- FI-85-2D: 1.0×10^{-4} M Al

Figure 17. Cumulative removal of K from silica prepared by the addition of $\text{Al}_2(\text{SO}_4)_3$ as a function of HCl concentration.

- a. FI-85-3: 5.0×10^{-4} M Al
- FI-85-4: 4.0×10^{-4} M Al
- FI-85-5: 3.0×10^{-4} M Al
- FI-85-6: 2.5×10^{-4} M Al
- b. FI-85-7: 2.0×10^{-4} M Al
- FI-85-8: 1.5×10^{-4} M Al
- FI-85-9: 1.0×10^{-4} M Al

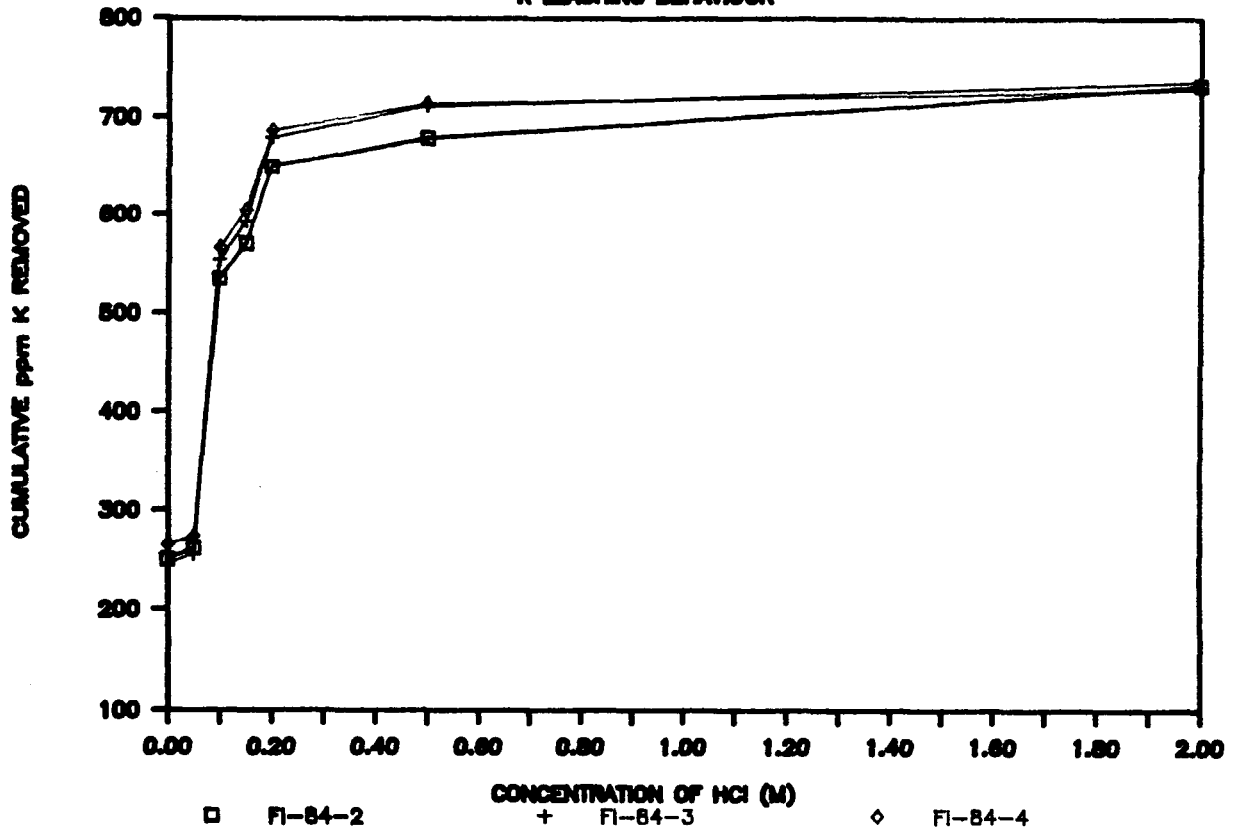
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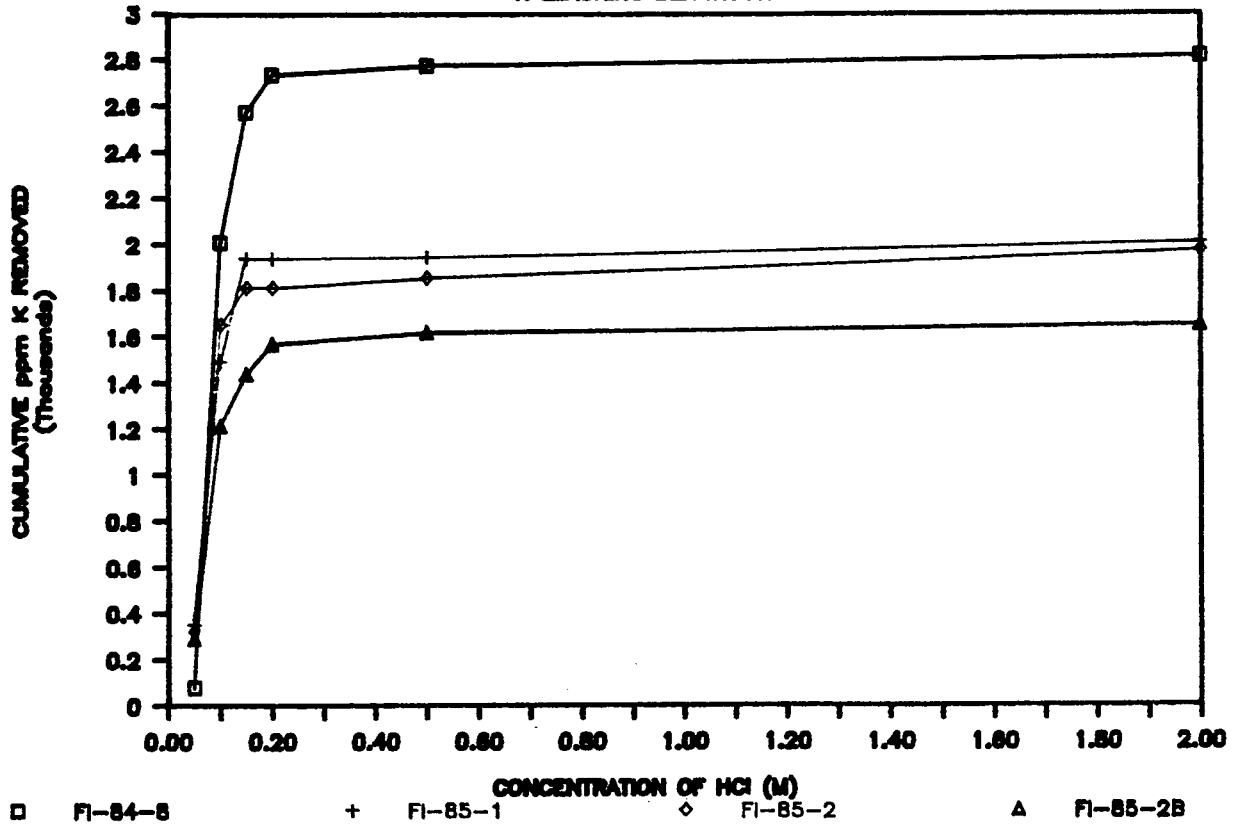
GEOTHERMAL SILICA PROJECT

K LEACHING BEHAVIOUR



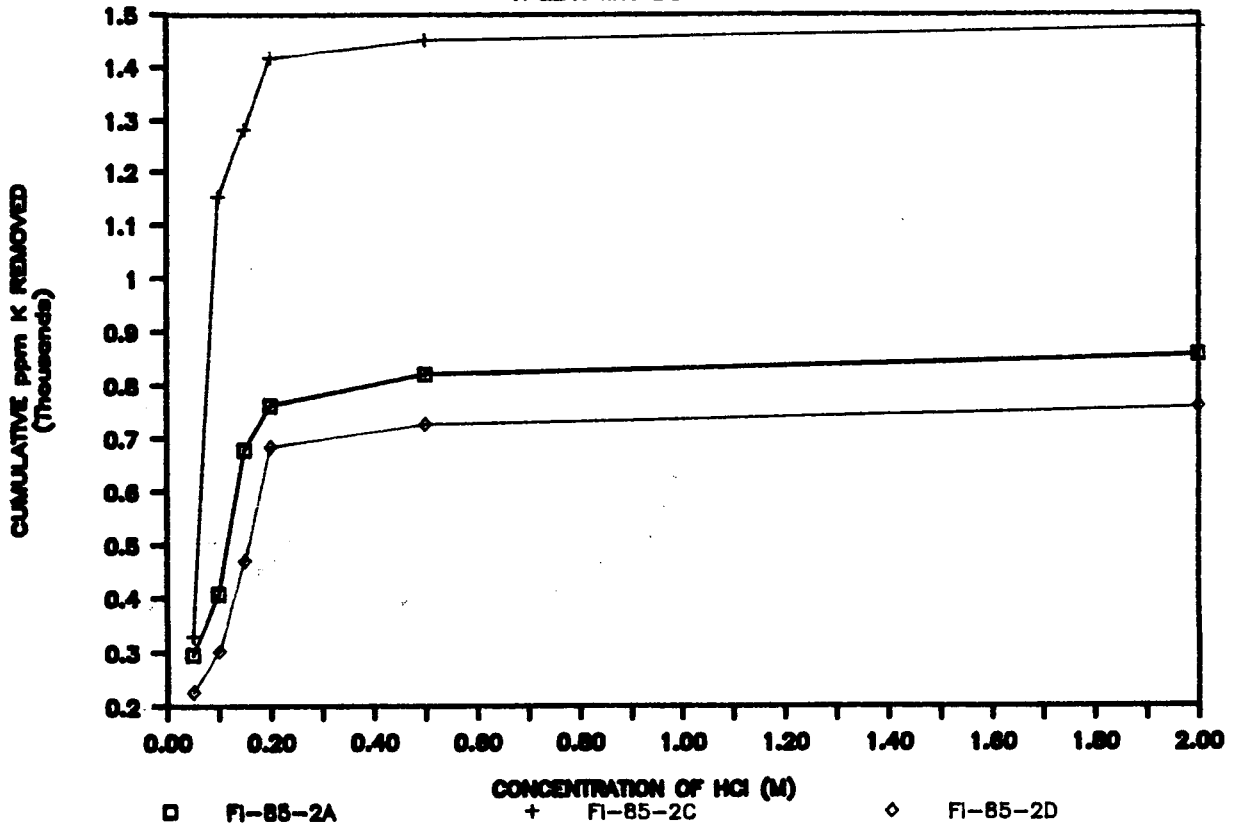
GEOTHERMAL SILICA PROJECT

K LEACHING BEHAVIOUR



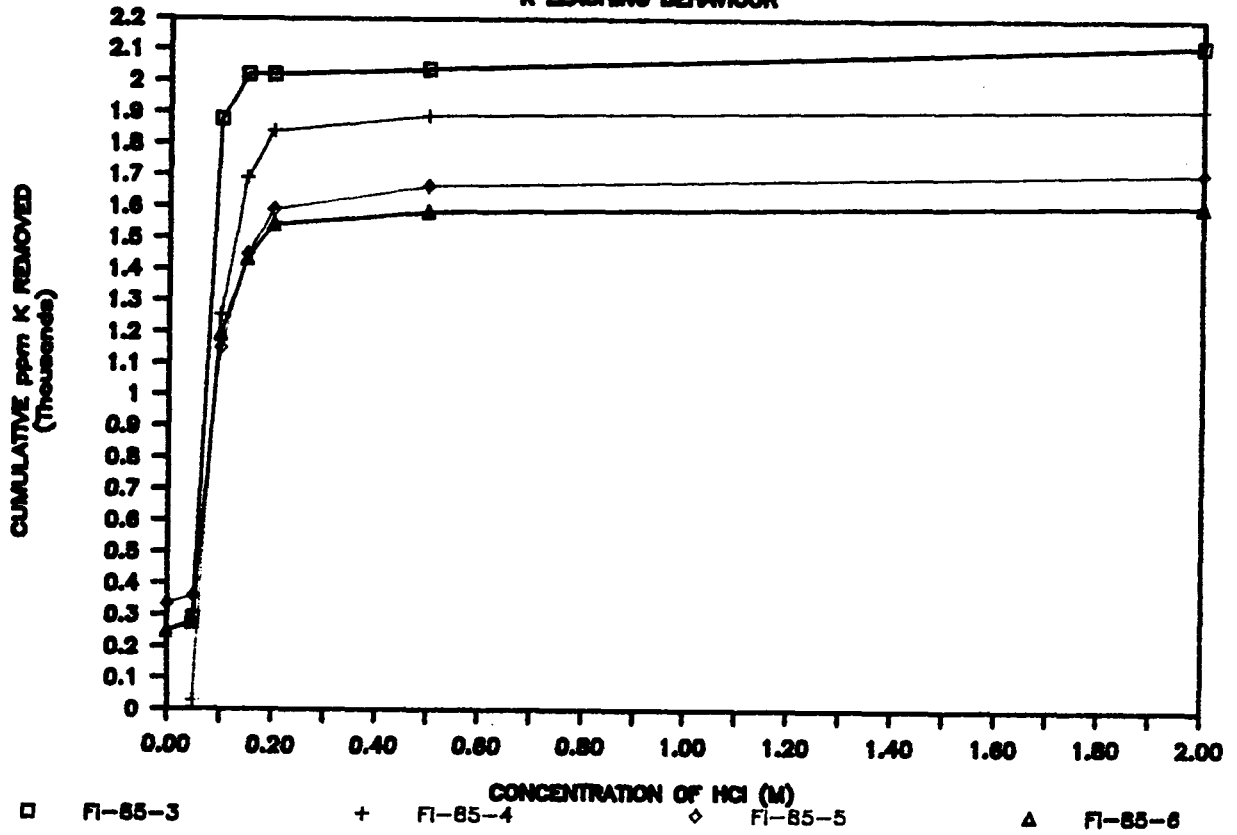
GEOTHERMAL SILICA PROJECT

K LEACHING BEHAVIOUR



GEOTHERMAL SILICA PROJECT

K LEACHING BEHAVIOUR



GEOTHERMAL SILICA PROJECT

K LEACHING BEHAVIOUR

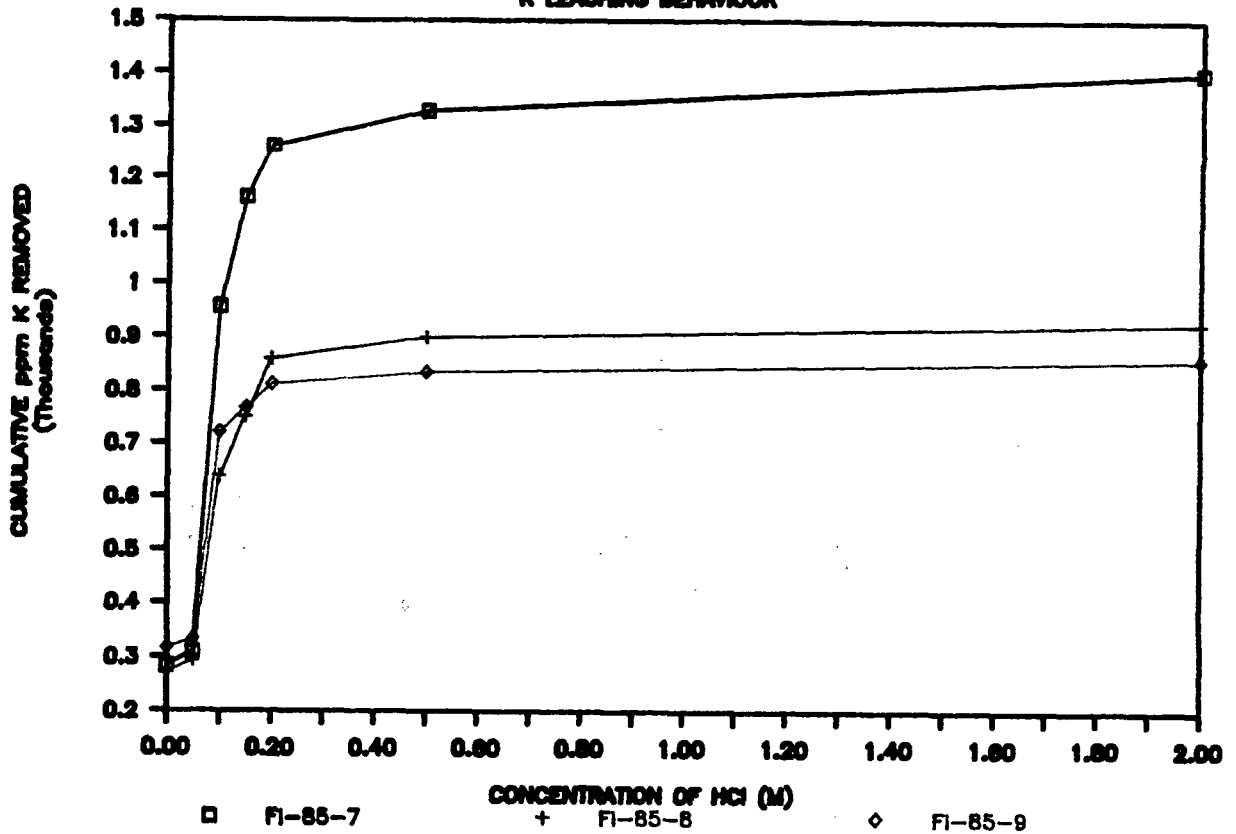


Figure 18. Cumulative removal of K from silica prepared by the addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

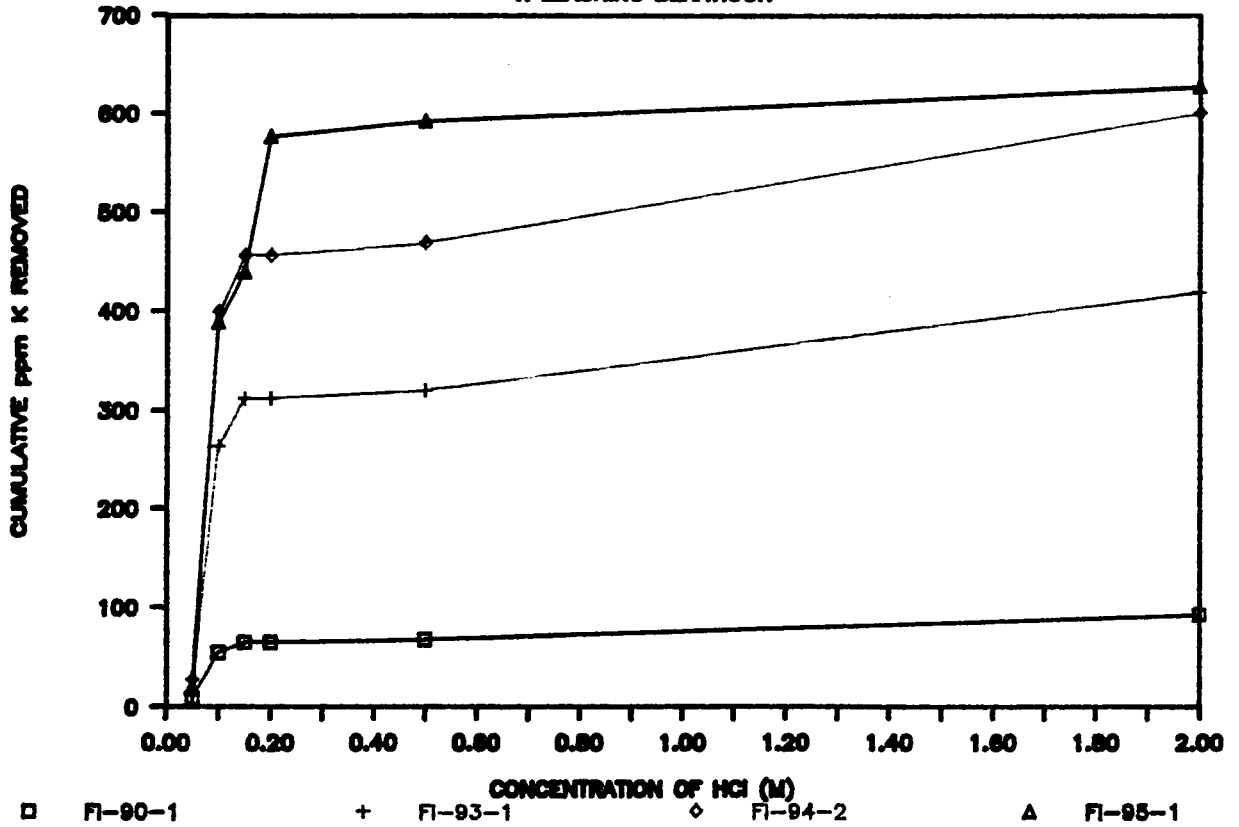
- FI-90-1: 1.25 X 10E-4 M Fe(III), and rinsed with distilled deionized (d.d.)
- FI-93-1: 2.5 X 10E-4 M Fe(III), not rinsed
- FI-94-2: 2.5 X 10E-4 M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant
- FI-95-1: 1.5 X 10E-4 M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant, and rinsed with d.d. H_2O

Figure 19. Cumulative removal of K from silica deposits from geothermal brines at HGP-A as a function of HCl concentration.

- a. X-29-1: silica precipitated by addition of NaOH to spent brine, final pH \geq 9.0
 - X-29-4: silica precipitated by addition of 2.5 X 10E-4 M Fe(III) to unflashed brine at pH = 8.0
 - X-29-5: silica precipitated by addition of 2.5 X 10E-4 M Al to unflashed brine at pH = 8.0
- b. X-29-2: silica deposited by natural precipitation in spent brine pH \sim 7.5
 - X-29-3: silica scale deposit from turbine nozzle inlet

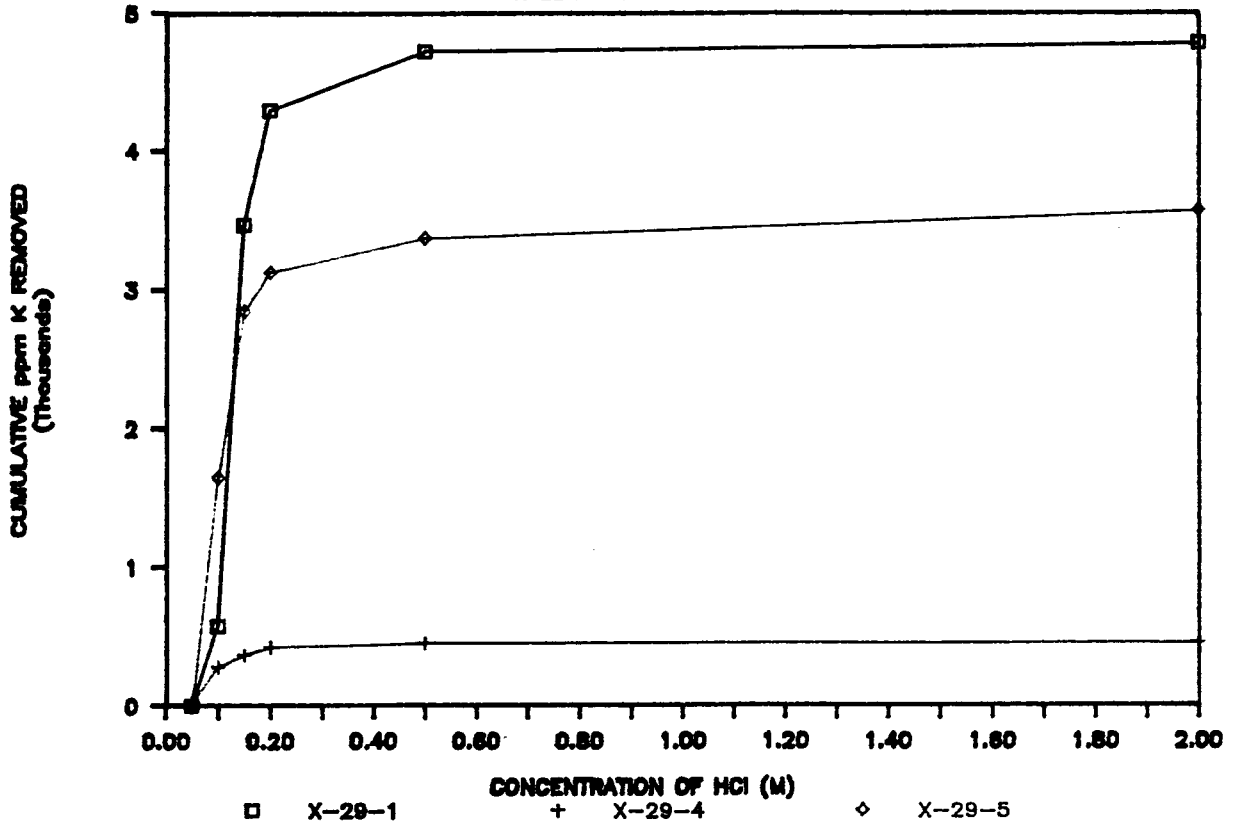
GEOHERMAL SILICA PROJECT

K LEACHING BEHAVIOUR



GEOTHERMAL SILICA PROJECT

K LEACHING BEHAVIOUR



GEOTHERMAL SILICA PROJECT

K LEACHING BEHAVIOUR

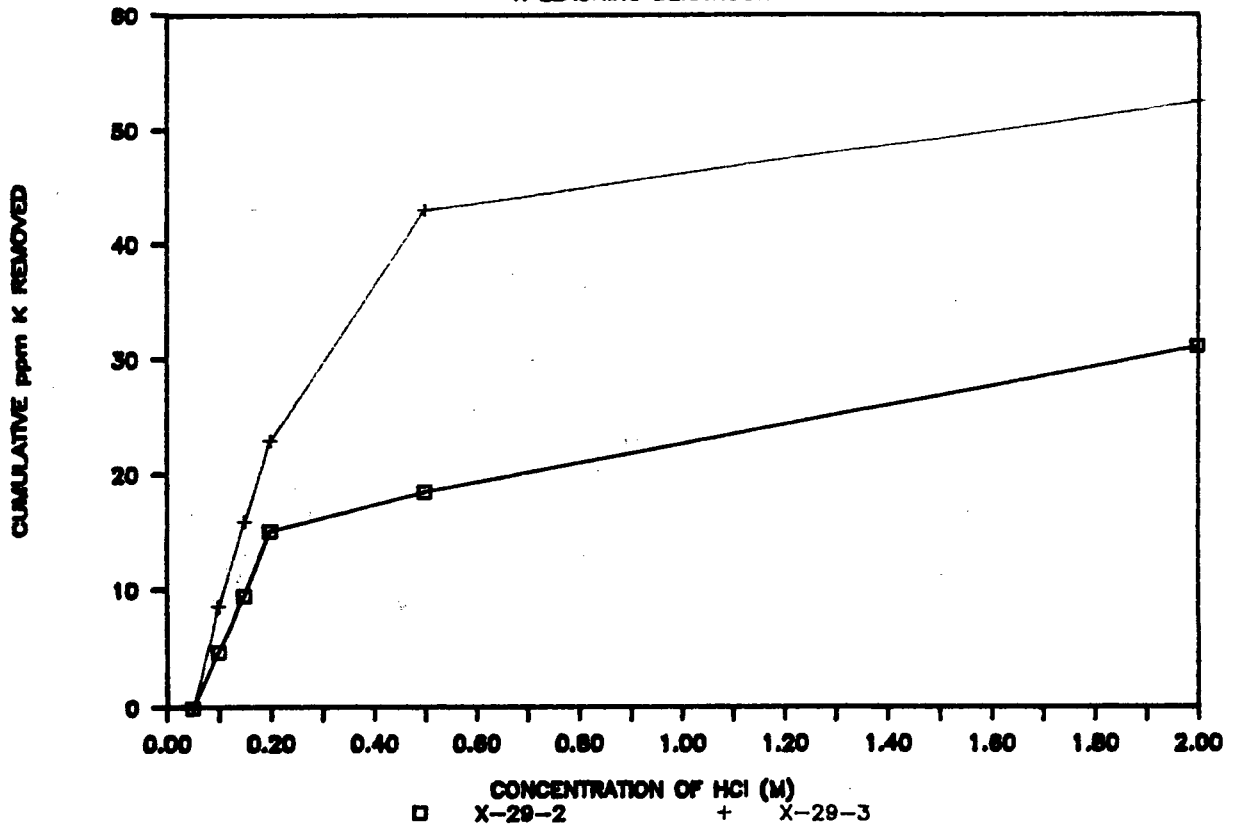


TABLE 7

CUMULATIVE REMOVAL OF Na FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.20	0.50	2.00
	Concentration of Na (in ppm)						
FI-84-1B	105333.5	2278.0	110.0	20.2	31.6	16.4	20.6
cum.	105333.5	107611.5	107721.5	107741.7	107773.3	107789.7	107810.3
FI-84-2	132500.0	3450.0	318.0	20.3	28.0	10.6	16.1
cum.	132500.0	135950.0	136268.0	136288.3	136316.3	136326.9	136343.0
FI-84-3	128079.0	2709.5	289.0	21.1	31.1	16.0	13.3
cum.	128079.0	130788.5	131077.5	131098.6	131129.7	131145.7	131159.0
FI-84-4	142250.0	2525.0	369.0	15.2	35.1	7.9	5.6
cum.	142250.0	144775.0	145144.0	145159.2	145194.3	145202.2	145207.8
FI-84-5	123148.0	1565.0	124.0	12.5	26.0	0.0	6.9
cum.	123148.0	124713.0	124837.0	124849.5	124875.5	124875.5	124882.4
FI-84-6	128182.0	1794.0	117.0	8.6	25.3	0.0	7.9
cum.	128182.0	129976.0	130093.0	130101.6	130126.9	130126.9	130134.8
FI-84-7	150485.0	1903.0	80.7	0.0	15.0	0.0	0.0
cum.	150485.0	152388.0	152468.7	152468.7	152483.7	152483.7	152483.7
FI-84-8		38775.5	2070.0	88.6	22.8	14.7	54.9
cum.		38775.5	40845.5	40934.1	40956.9	40971.6	41026.5
FI-85-1		179047.5	3990.0	73.9	27.6	19.6	42.7
cum.		179047.5	183037.5	183111.4	183139.0	183158.6	183201.3
FI-85-2		164186.0	5440.0	89.6	29.1	22.0	20.4
cum.		164186.0	169626.0	169715.6	169744.7	169766.7	169787.1
FI-85-2A		145815.0	4760.0	121.0	30.8	26.5	25.1
cum.		145815.0	150575.0	150696.0	150726.8	150753.3	150778.4
FI-85-2B		139726.0	4450.0	79.1	32.3	21.5	22.7
cum.		139726.0	144176.0	144255.1	144287.4	144308.9	144331.6
FI-85-2C		157971.0	3560.0	52.5	18.3	7.6	6.4
cum.		157971.0	161531.0	161583.5	161601.8	161609.4	161615.8
FI-85-2D		113785.0	2590.0	101.0	81.7	55.4	59.4
cum.		113785.0	116375.0	116476.0	116557.7	116613.1	116672.5
FI-85-3		151626.0	2090.0	65.7	47.1	48.6	89.3
cum.		151626.0	153716.0	153781.7	153828.8	153877.4	153966.7
FI-85-4	153755.0	5988.0	809.0	55.7	28.8	16.4	15.8
cum.	153755.0	159743.0	160552.0	160607.7	160636.5	160652.9	160668.7

TABLE 7

CUMULATIVE REMOVAL OF Na FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.20	0.50	2.00
	Concentration of Na (in ppm)						
FI-85-5	167323.0	4586.5	597.0	92.1	73.4	94.6	64.4
cum.	167323.0	171909.5	172506.5	172598.6	172672.0	172766.6	172831.0
FI-85-6	131128.5	5350.0	505.0	41.8	33.8	17.7	22.2
cum.	131128.5	136478.5	136983.5	137025.3	137059.1	137076.8	137099.0
FI-85-7	141213.5	4581.5	360.0	75.7	63.4	53.2	49.4
cum.	141213.5	145795.0	146155.0	146230.7	146294.1	146347.3	146396.7
FI-85-8	150680.5	3197.5	248.0	121.0	132.0	118.0	0.2
cum.	150680.5	153878.0	154126.0	154247.0	154379.0	154497.0	154497.2
FI-85-9	164052.5	2225.5	81.1	3.2	6.7	0.0	0.0
cum.	164052.5	166278.0	166359.1	166362.3	166369.0	166369.0	166369.0
FI-90-1		2340.0	196.0	48.2	68.1	26.5	76.6
cum.		2340.0	2536.0	2584.2	2652.3	2678.8	2755.4
FI-93-1		5314.0	555.0	70.0	97.2	21.7	49.4
cum.		5314.0	5869.0	5939.0	6036.2	6057.9	6107.3
FI-94-2		16842.0	662.0	55.8	85.0	20.0	50.5
cum.		16842.0	17504.0	17559.8	17644.8	17664.8	17715.3
FI-95-1		13942.5	374.0	60.8	100.0	37.0	80.7
cum.		13942.5	14316.5	14377.3	14477.3	14514.3	14595.0
X-29-1		18224.0	10240.0	10052.0	1211.0	283.0	99.0
cum.		18408.0	28648.0	38700.0	39911.0	40194.0	40293.0
X-29-2		60.0	25.5	23.0	24.7	21.1	36.3
cum.		60.0	85.5	108.5	133.2	154.3	190.6
X-29-3		127.5	27.9	25.0	28.3	27.3	32.6
cum.		127.5	155.4	180.4	208.7	236.0	268.6
X-29-4		16428.0	403.0	27.8	24.9	1.2	2.5
cum.		16428.0	16831.5	16859.3	16884.2	16885.4	16887.9
X-29-5		42961.0	1513.0	350.0	16.9	17.8	34.7
cum.		42961.0	44474.0	44824.0	44840.9	44858.7	44893.4

Figure 20: Cumulative removal of Na from silica prepared by addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

FI-84-2: 4.0 X 10E-4 M Fe(III)
 FI-84-4: 2.5 X 10E-4 M Fe(III)
 FI-84-7: 1.0 X 10E-4 M Fe(III)

Figure 21; Cumulative removal of Na from silica prepared by addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

a. FI-84-1b: 5.0 X 10E-4 M Fe(III)
 b. FI-84-3: 3.0 X 10E-4 M Fe(III)
 FI-84-5: 2.0 X 10E-4 M Fe(III)
 FI-84-6: 1.5 X 10E-4 M Fe(III)

Figure 22. Cumulative removal of Na from silica prepared by addition of $\text{KAl}(\text{SO}_4)_2$ as a function of HCl concentration.

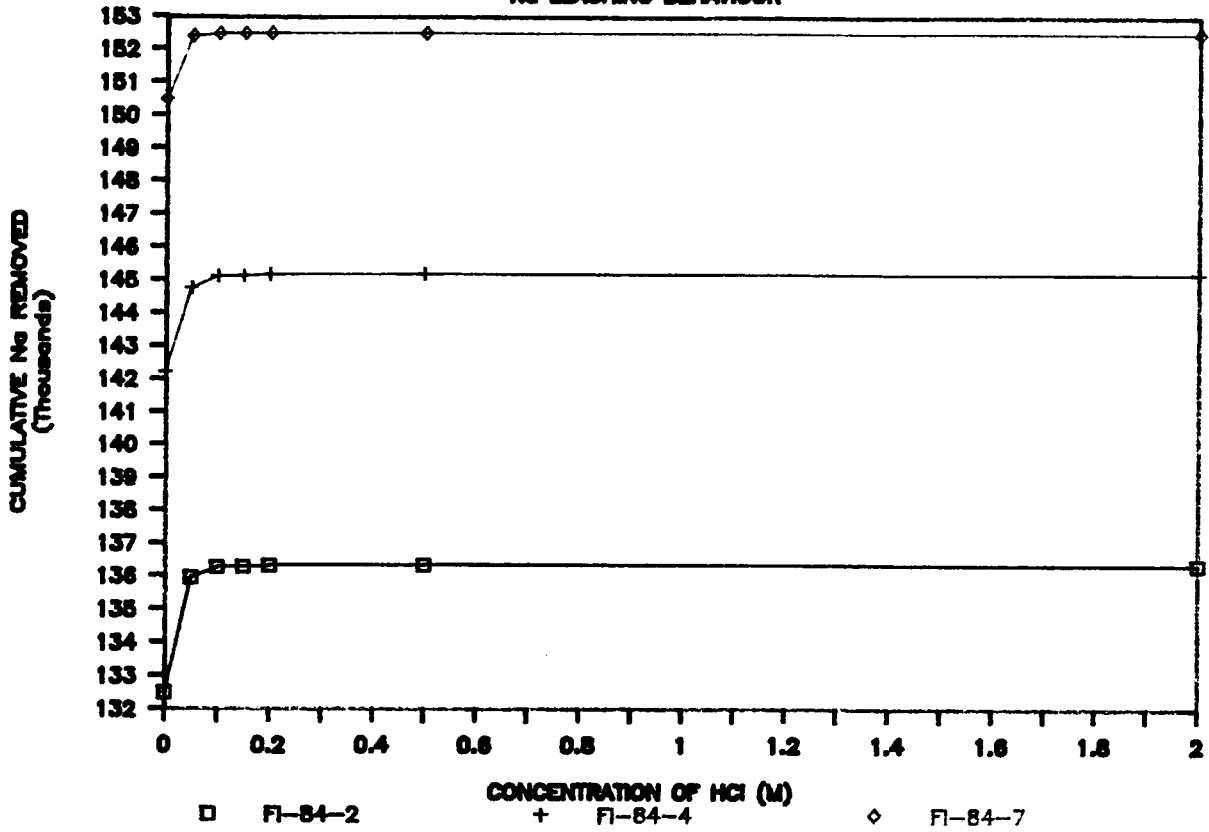
a. FI-85-1: 4.0 X 10E-4 M Al
 FI-85-2: 3.0 X 10E-4 M Al
 FI-85-2C: 1.5 X 10E-4 M Al
 b. FI-84-8: 5.0 X 10E-4 M Al
 FI-85-2A: 2.5 X 10E-4 M Al
 FI-85-2B: 2.0 X 10E-4 M Al
 FI-85-2D: 1.0 X 10E-4 M Al

Figure 23: Cumulative removal of Na from silica prepared by addition of $\text{Al}_2(\text{SO}_4)_3$ as a function of HCl concentration.

a. FI-85-5: 3.0 X 10E-4 M Al
 FI-85-6: 2.5 X 10E-4 M Al
 FI-85-7: 2.0 X 10E-4 M Al
 FI-85-9: 1.0 X 10E-4 M Al
 b. FI-85-3: 5.0 X 10E-4 M Al
 FI-85-4: 4.0 X 10E-4 M Al
 FI-85-8: 1.5 X 10E-4 M Al

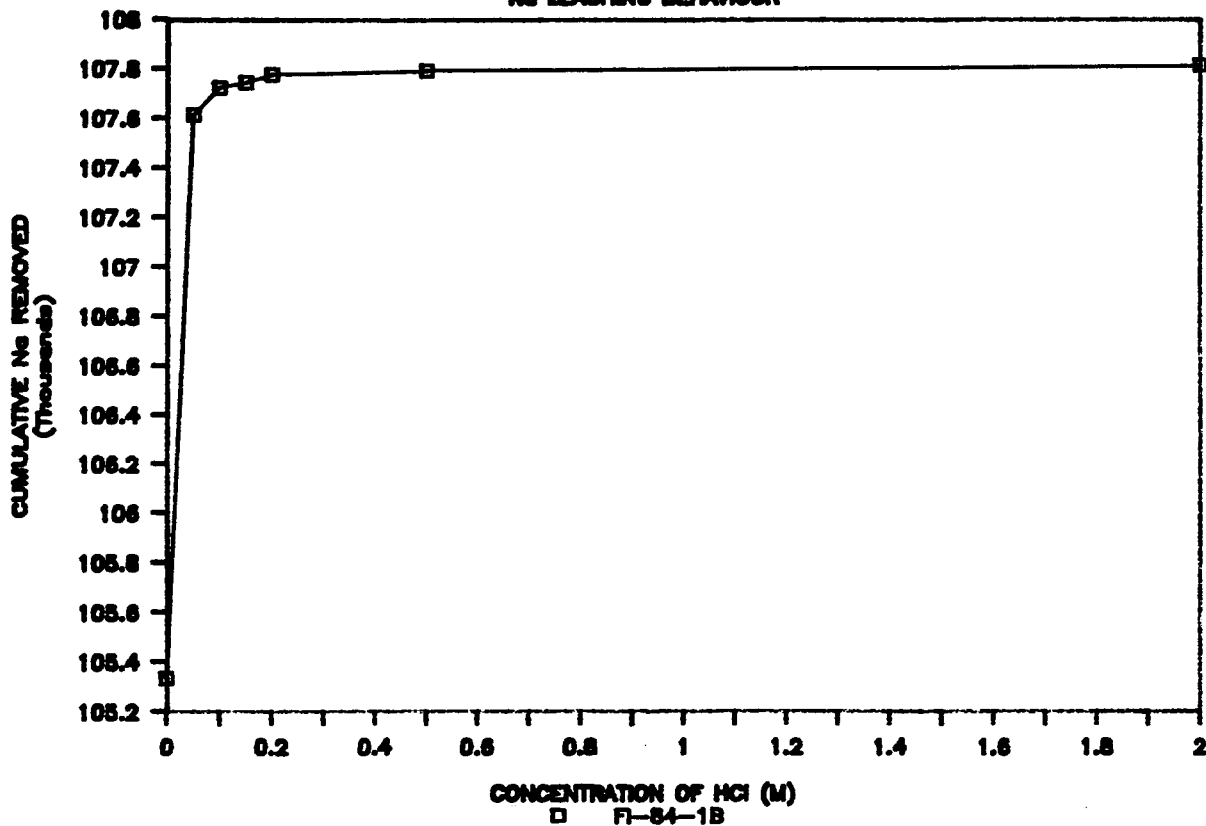
GEOTHERMAL SILICA PROJECT

No LEACHING BEHAVIOUR



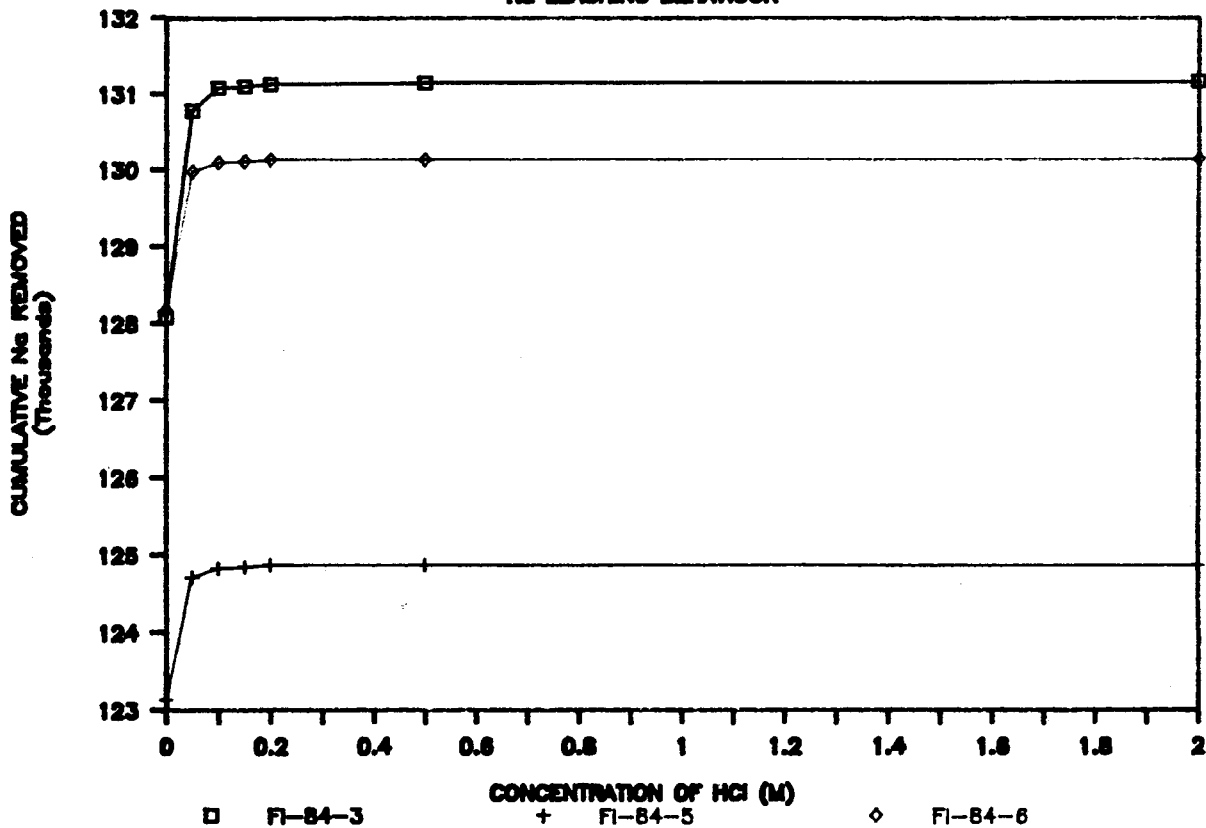
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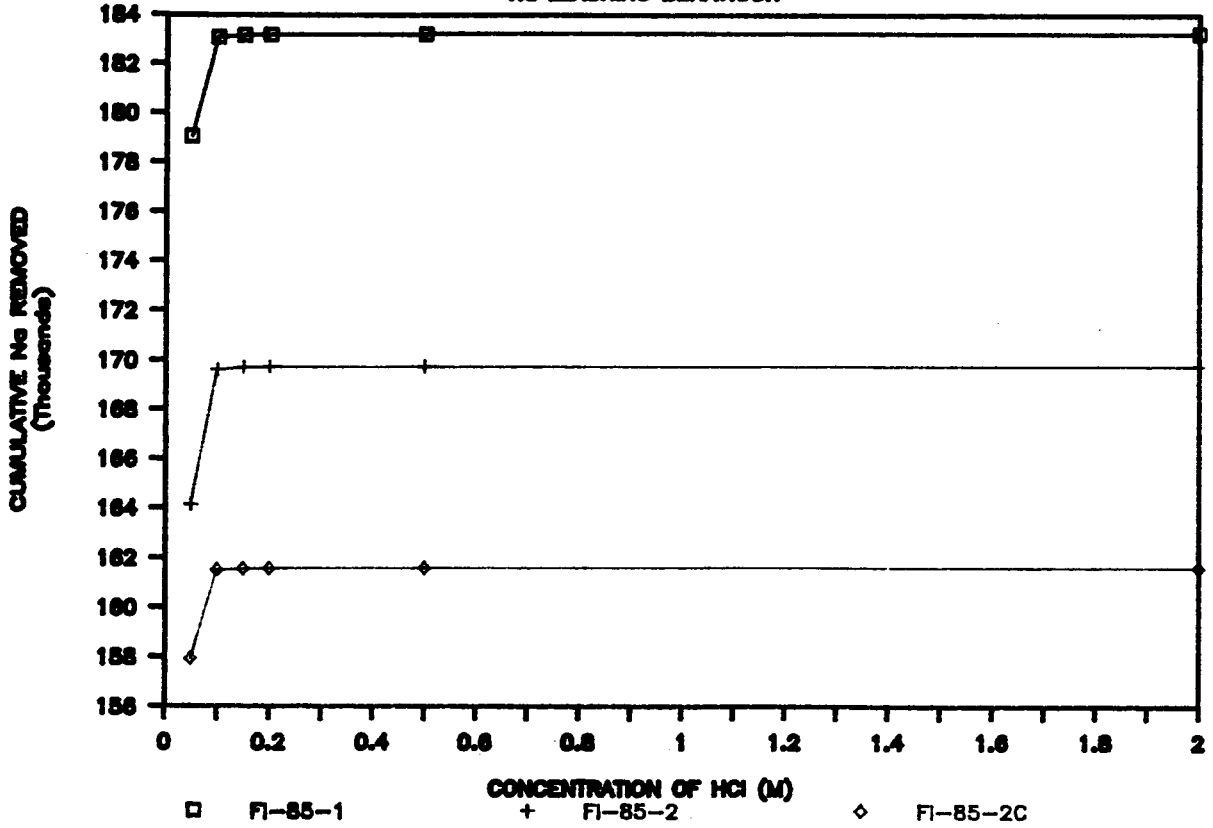
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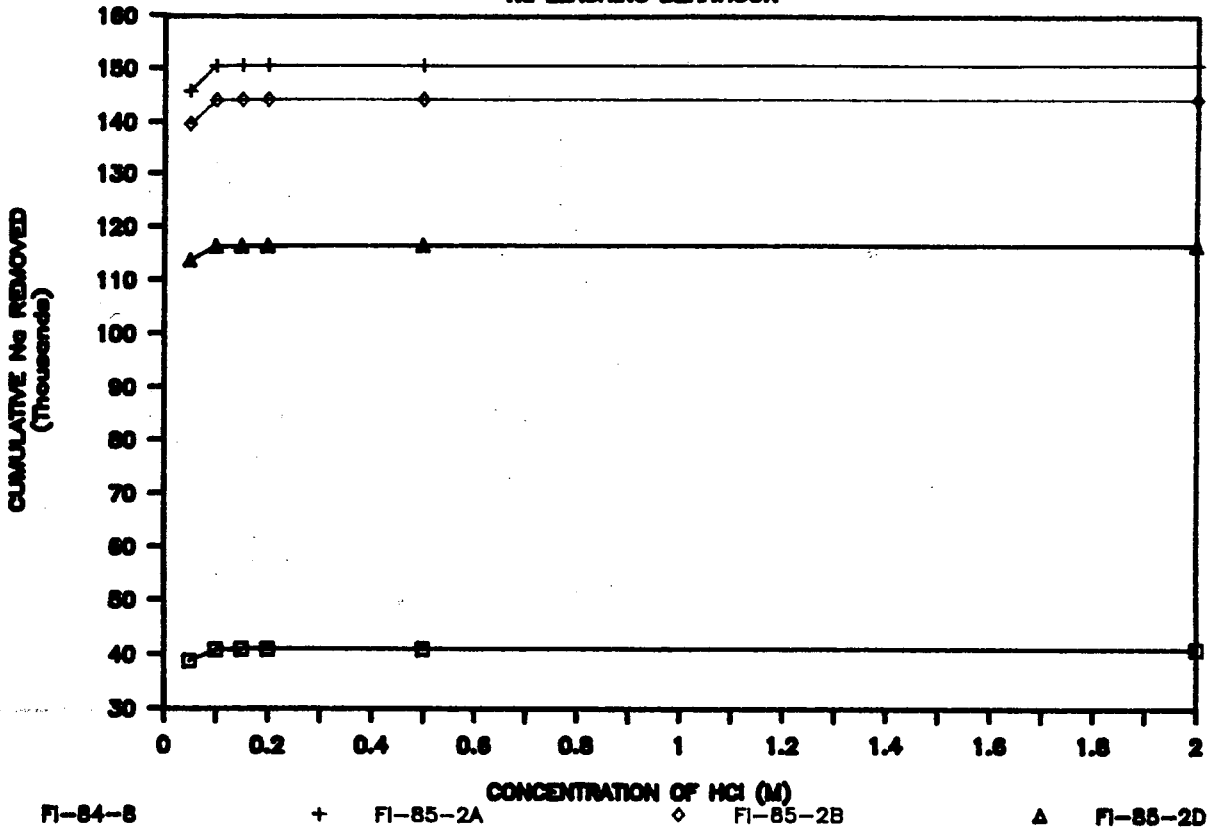
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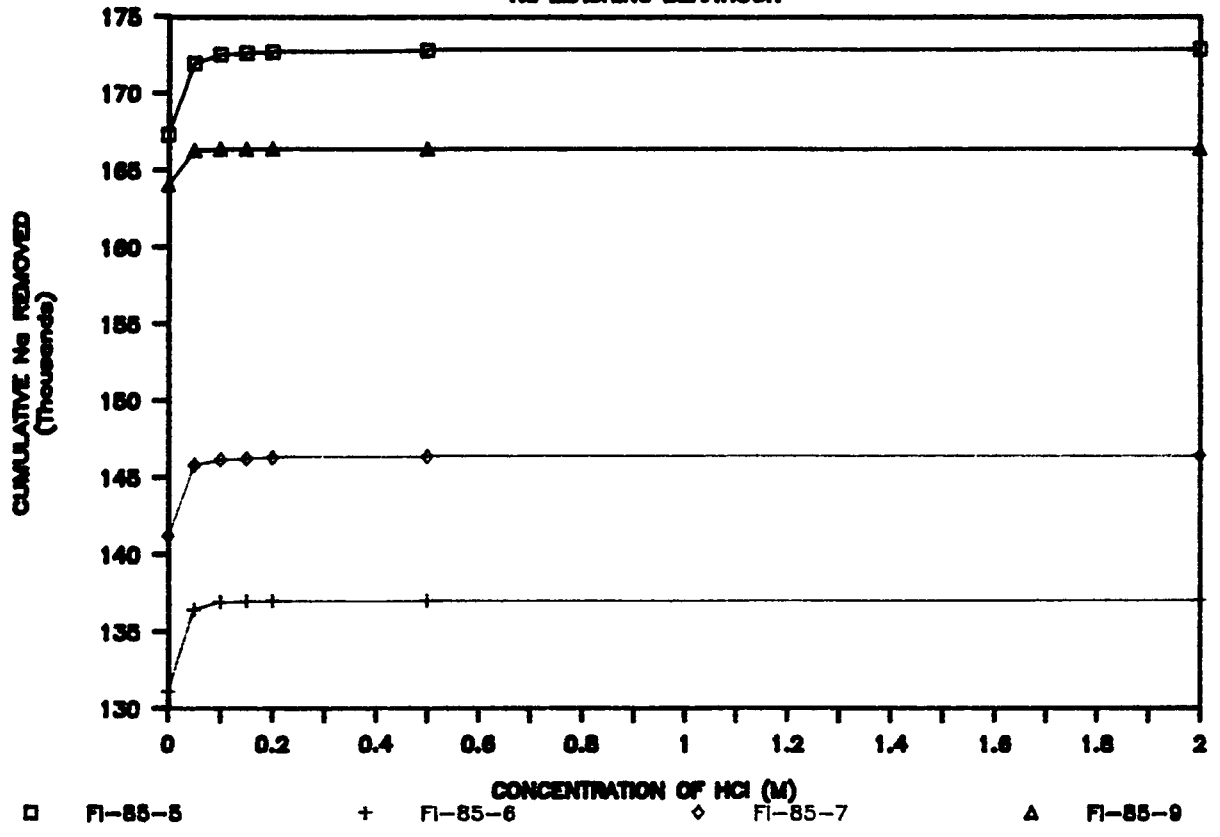
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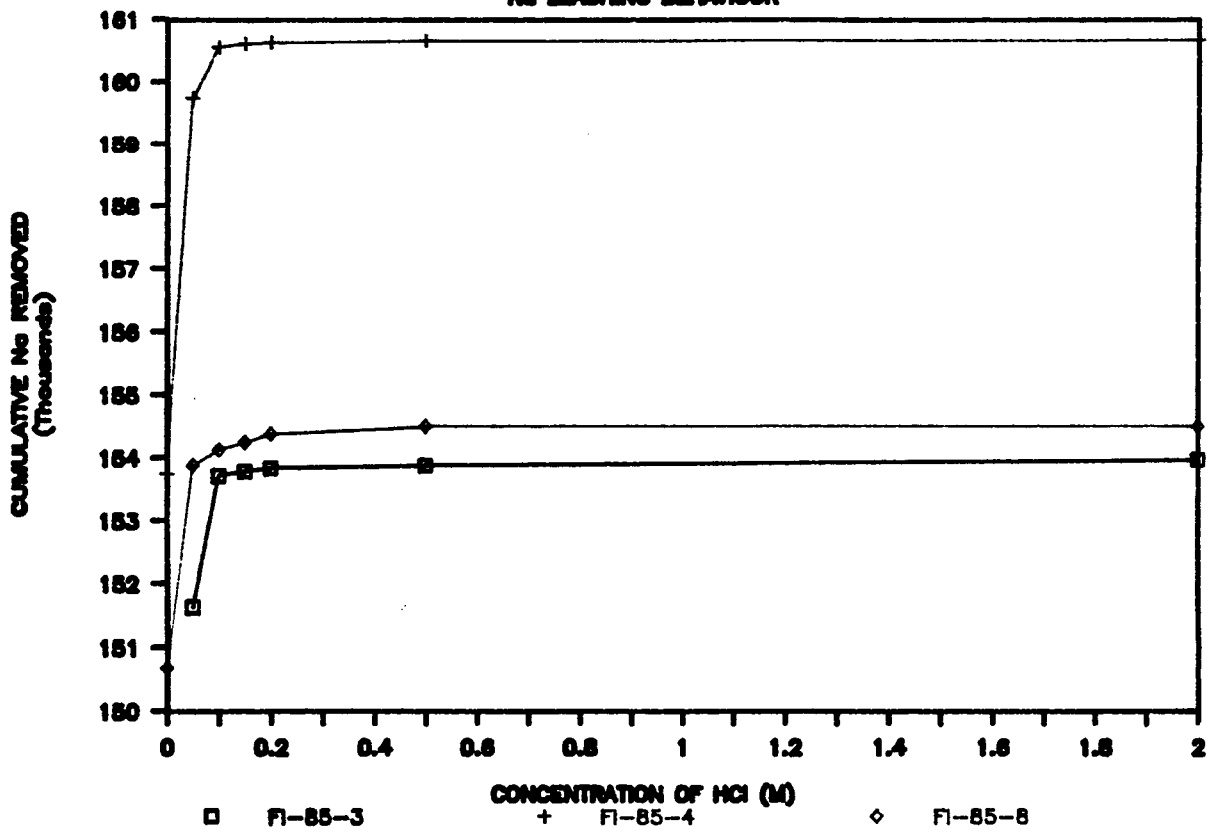


Figure 24: Cumulative removal of Na from silica prepared by the addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

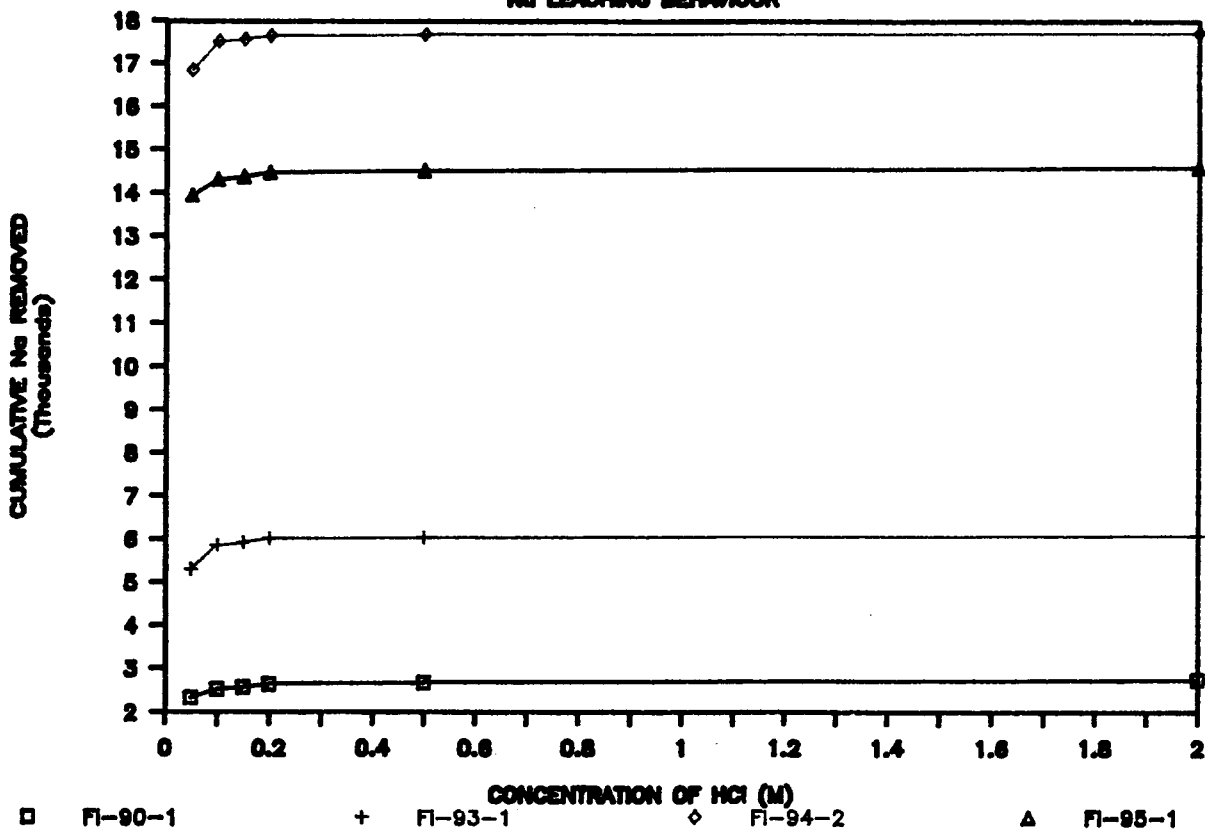
- FI-90-1: 1.25×10^{-4} M Fe(III), and rinsed with distilled deionized (d.d.)
- FI-93-1: 2.5×10^{-4} M Fe(III), not rinsed
- FI-94-2: 2.5×10^{-4} M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant
- FI-95-1: 1.5×10^{-4} M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant, and rinsed with d.d. H_2O

Figure 25: Cumulative removal of Na from silica deposits from geothermal fluids at HGP-A as a function of HCl concentration.

- a. X-29-1: silica precipitated by addition of NaOH to spent brine, final pH ≥ 9.0
- X-29-4: silica precipitated by addition of 2.5×10^{-4} M Fe(III) to unflashed brine at pH = 8.0
- X-29-5: silica precipitated by addition of 2.5×10^{-4} M Al to unflashed brine at pH = 8.0
- b. X-29-2: silica deposited by natural precipitation in spent brine pH ~ 7.5
- X-29-3: silica scale deposit from turbine nozzle inlet

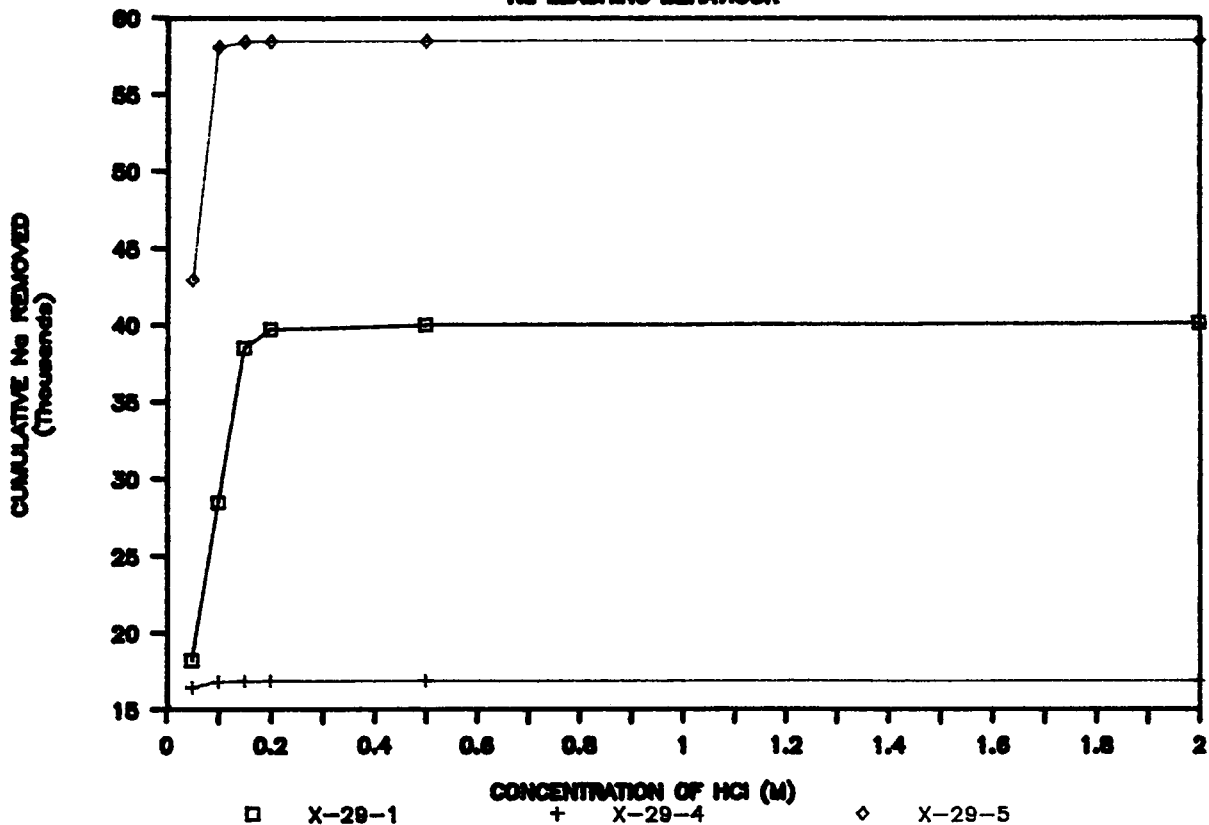
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Na LEACHING BEHAVIOUR



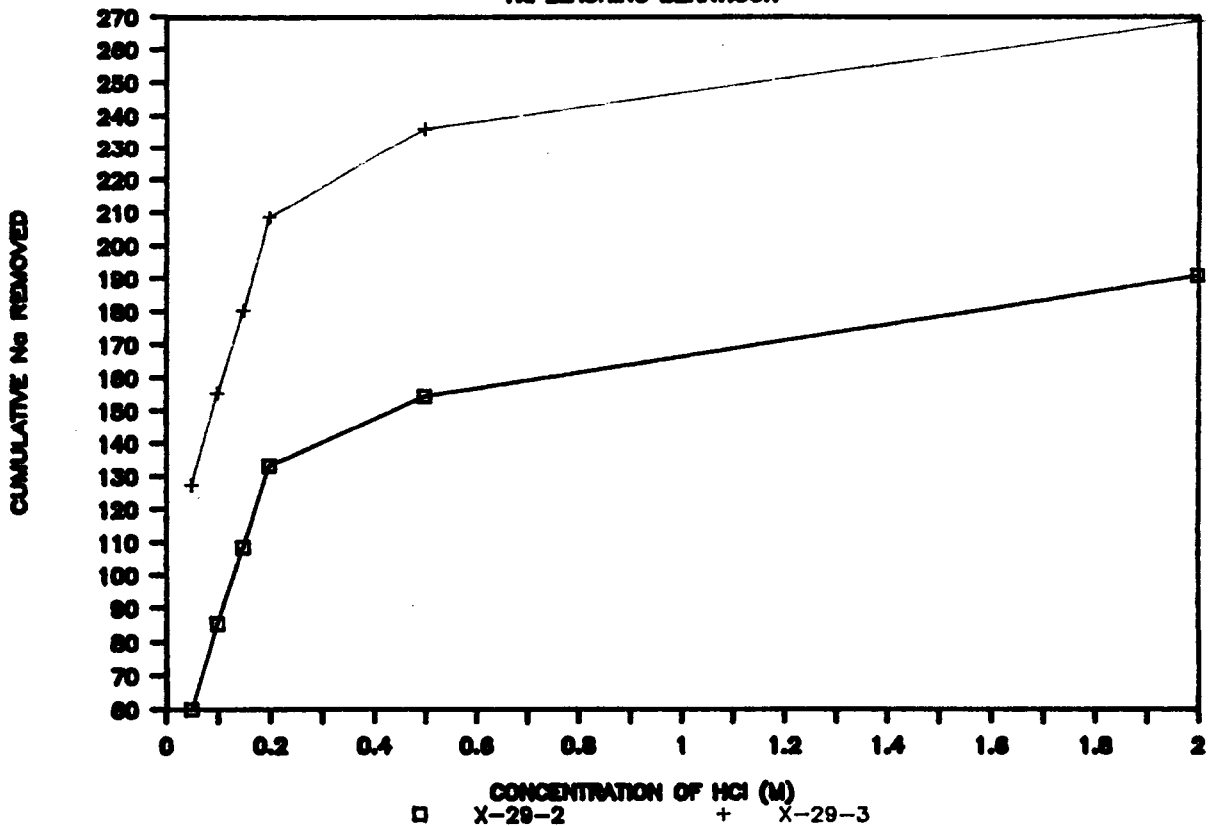
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employed reflects the rapid kinetics of this process as well as the fact that Na (as the most abundant cation in the brine) is present in large amounts as counter-ions at the electrical double layer of the silica surface.

Samples which deposited over extended time periods preferentially adsorb higher valence cations and effectively scavenge Ca and Mg; the mechanism of adsorption in this case is probably one of ion exchange at the active silica surface. Examination of the data in Table 2 reveals that both Ca and Mg achieve high enrichments relative to Na in the solid versus liquid phases due to higher charge to size ratios and in spite of their much lower abundances. This is further substantiated by the significantly greater concentration of Mg in X-29-3 as compared to X-29-2; the high Mg abundance most likely results from its greater charge to size ratio versus that of Ca and thus favors its adsorption, although it is the least abundant of the three cations discussed.

Samples X-29-1 which was precipitated by the addition of NaOH to spent brine was more difficult to leach free of Na than other enhanced precipitation samples. In this sample up to 0.15 M HCl was necessary to remove the majority of the Na. This points to the presence of Na in less accessible sites within the silica structure, and is confirmed by X-ray diffraction analysis. The diffraction pattern obtained indicates that the sample is primarily a calcium-carbonate-silicate of good crystallinity (e.g. highly ordered) (Brindley and Brown, 1980). In light of this information it is not surprising that some of the constituents of the sample are difficult to remove, particularly if they are involved in the structural arrangement of the mineral.

The two samples of natural scale which have been discussed briefly above also have quite similar Na concentrations in the solids prior to leaching. The two removal curves although similar in shape show that only 12 and 13% of the Na is leachable in X-29-2 and 29-3 respectively under the conditions of our experiments. The Na was incorporated slowly in these samples and is probably an integral part of the silicate structure. Although these samples are both primarily amorphous to X-rays, diffraction patterns suggests the presence of trace amounts of cristobalite and indicates that the structure of the silica has a certain degree of order that is absent in silica formed by precipitation in the presence of inorganic flocculating agents. Such an ordered structure is inherently more stable to acid attack and will then only release its constituents at a much slower rate or under more severe chemical conditions.

Calcium:

Comparison of the pre-leach compositional data presented in Table 1 with those for the cumulative removal of Ca shown in Table 8 reveals that between 61% and 94% of the Ca originally present in the unrinsed samples prepared by enhanced flocculation is removed by the HCl leachings. The samples which were rinsed at HGP-A prior to the chemical treatments carried out in our laboratory at HIG have significantly lower solid Ca concentrations than the unrinsed precipitates before leaching (see Table 1). The rinsed samples exhibit constant removals within analytical error (range 59.7-60.8%) of the approximately 5 mg/g Ca present. The identical efficiency of removal of Ca regardless of the presence or absence of a cationic surfactant supports the proposed mechanism previously proposed for the Fe behaviour in the presence of surfactants. The laurylammonium cation cannot attract divalent Ca electrostatically and affect its behaviour whereas it can, and most likely does, have a significant attraction for negatively charged Fe hydroxy complexes. Calculations by difference indicate that approximately 2-2.5 mg/g Ca remains in the silica after treatment. The removal of Ca from the latter samples is interesting in that the amount removed at HIG appears to be significantly less than that removed by the on-site leachings. Data for the on-site leachings have been previously presented in Figure 4 and 5. The data in Figure 5 are directly comparable to

TABLE 8

CUMULATIVE REMOVAL OF Ca FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.35	0.50	2.00
	Concentration of Ca (in ppm)						
FI-84-1B	7740.0	2140.0	168.0	601.0	52.0	33.1	44.6
cum.	7740.0	9880.0	10048.0	10649.0	10701.0	10734.1	10778.7
FI-84-2	7240.0	3240.0	654.0	97.0	148.0	69.0	147.0
cum.	7240.0	10480.0	11134.0	11231.0	11379.0	11448.0	11595.0
FI-84-3	7390.0	3030.0	512.0	102.0	147.0	64.4	71.3
cum.	7390.0	10420.0	10932.0	11034.0	11181.0	11245.4	11316.7
FI-84-4	8460.0	2450.0	451.0	102.0	147.0	67.7	62.7
cum.	8460.0	10910.0	11361.0	11463.0	11610.0	11677.7	11740.4
FI-84-5	7120.0	3980.0	179.0	74.9	112.0	52.5	109.0
cum.	7120.0	11100.0	11279.0	11353.9	11465.9	11518.4	11627.4
FI-84-6	7020.0	3660.0	183.0	67.7	114.0	49.0	112.0
cum.	7020.0	10680.0	10863.0	10930.7	11044.7	11093.7	11205.7
FI-84-7	9370.0	3430.0	90.6	36.0	60.8	28.7	63.5
cum.	9370.0	12800.0	12890.6	12926.6	12987.4	13016.1	13079.6
FI-84-8		5650.0	2110.0	274.0	313.0	46.3	136.0
cum.		5650.0	7760.0	8034.0	8347.0	8393.3	8529.3
FI-85-1		9480.0	1690.0	230.0	515.0	54.4	146.0
cum.		9480.0	11170.0	11400.0	11915.0	11969.4	12115.4
FI-85-2		9660.0	1040.0	137.0	315.0	36.4	75.6
cum.		9660.0	10700.0	10837.0	11152.0	11188.4	11264.0
FI-85-2A		9280.0	757.0	292.0	221.0	55.8	60.9
cum.		9280.0	10037.0	10329.0	10550.0	10605.8	10666.7
FI-85-2B		6890.0	1170.0	743.0	852.0	168.0	198.0
cum.		6890.0	8060.0	8803.0	9655.0	9823.0	10021.0
FI-85-2C		10620.0	447.0	145.0	315.0	52.2	64.6
cum.		10620.0	11067.0	11212.0	11527.0	11579.2	11643.8
FI-85-2D		5990.0	594.0	286.0	636.0	118.0	138.0
cum.		5990.0	6584.0	6870.0	7506.0	7624.0	7762.0
FI-85-3		10960.0	1670.0	104.0	204.0	31.8	95.3
cum.		10960.0	12630.0	12734.0	12938.0	12969.8	13065.1
FI-85-4	7780.0	3350.0	1220.0	199.0	203.0	70.3	81.1
cum.	7780.0	11130.0	12350.0	12549.0	12752.0	12822.3	12903.4

TABLE 8

CUMULATIVE REMOVAL OF Ca FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.35	0.50	2.00
	Concentration of Ca (in ppm)						
FI-85-5	7790.0	3590.0	1670.0	280.0	413.0	132.0	157.0
cum.	7790.0	11380.0	13050.0	13330.0	13743.0	13875.0	14032.0
FI-85-6	7730.0	2720.0	700.0	122.0	175.0	61.1	81.8
cum.	7730.0	10450.0	11150.0	11272.0	11447.0	11508.1	11589.9
FI-85-7	7680.0	1820.0	623.0	146.0	267.0	130.0	149.0
cum.	7680.0	9500.0	10123.0	10269.0	10536.0	10666.0	10815.0
FI-85-8	8840.0	1900.0	429.0	117.0	377.0	105.0	140.0
cum.	8840.0	10740.0	11169.0	11286.0	11663.0	11768.0	11908.0
FI-85-9	11000.0	2350.0	370.0	69.2	192.0	81.7	172.0
cum.	11000.0	13350.0	13720.0	13789.2	13981.2	14062.9	14234.9
FI-90-1		2490.0	134.0	35.1	54.8	21.4	70.4
cum.		2490.0	2624.0	2659.1	2713.9	2735.3	2805.7
FI-93-1		2470.0	431.0	74.4	121.0	24.6	63.9
cum.		2470.0	2901.0	2975.4	3096.4	3121.0	3184.9
FI-94-2		2970.0	334.0	62.5	107.0	22.1	74.0
cum.		2970.0	3304.0	3366.5	3473.5	3495.6	3569.6
FI-95-1		2810.0	202.0	42.1	74.9	16.4	76.3
cum.		2810.0	3012.0	3054.1	3129.0	3145.4	3221.7
X-29-1		199.0	8085.0	51617.0	16791.0	34826.0	3980.0
cum.		199.0	8284.0	59901.0	76692.0	111518.0	115498.0
X-29-2		322.0	12.9	12.9	11.6	6.4	20.1
cum.		322.0	334.9	347.8	359.4	365.8	385.9
X-29-3		3525.0	179.0	124.0	68.0	34.0	113.8
cum.		3525.0	3704.0	3828.0	3896.0	3930.0	4043.8
X-29-4		4121.0	782.1	442.9	457.1	172.1	235.0
cum.		4121.0	4903.1	5346.0	5803.1	5975.2	6210.2
X-29-5		3932.0	2005.0	709.0	544.0	118.0	471.0
cum.		3932.0	5937.0	6646.0	7190.0	7308.0	7779.0

Figure 26. Cumulative removal of Ca from silica prepared by addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

FI-90-1: 1.25 X 10E-4 M Fe(III), and rinsed with distilled deionized (d.d.)
FI-93-1: 2.5 X 10E-4 M Fe(III), not rinsed
FI-94-2: 2.5 X 10E-4 M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant
FI-95-1: 1.5 X 10E-4 M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant, and rinsed with d.d. H_2O

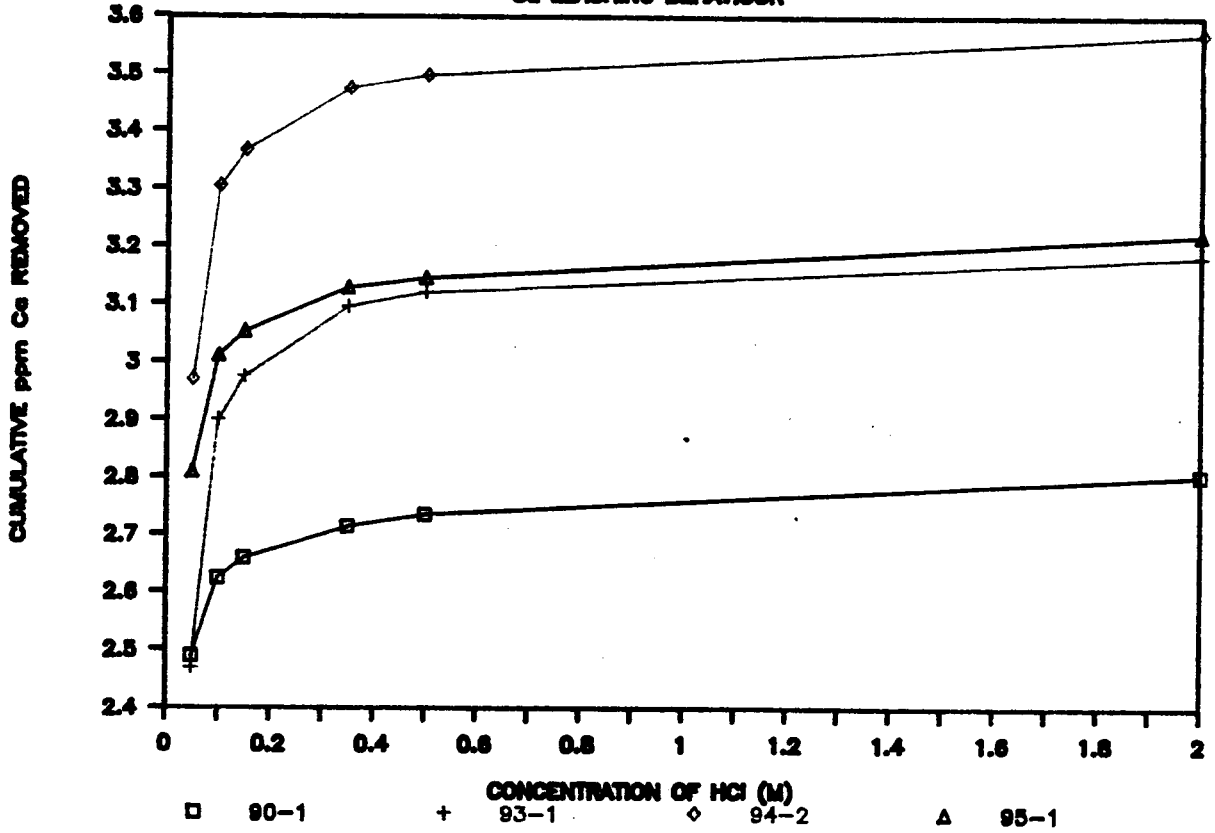
Figure 27. Cumulative removal of Ca from silica prepared by the addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

a. FI-84-1B: 5.0 X 10E-4 M Fe(III)
FI-84-2: 4.0 X 10E-4 M Fe(III)
FI-84-3: 3.0 X 10E-4 M Fe(III)
FI-84-4: 2.5 X 10E-4 M Fe(III)

b. FI-84-5: 2.0 X 10E-4 M Fe(III)
FI-84-6: 1.5 X 10E-4 M Fe(III)
FI-84-7: 1.0 X 10E-4 M Fe(III)

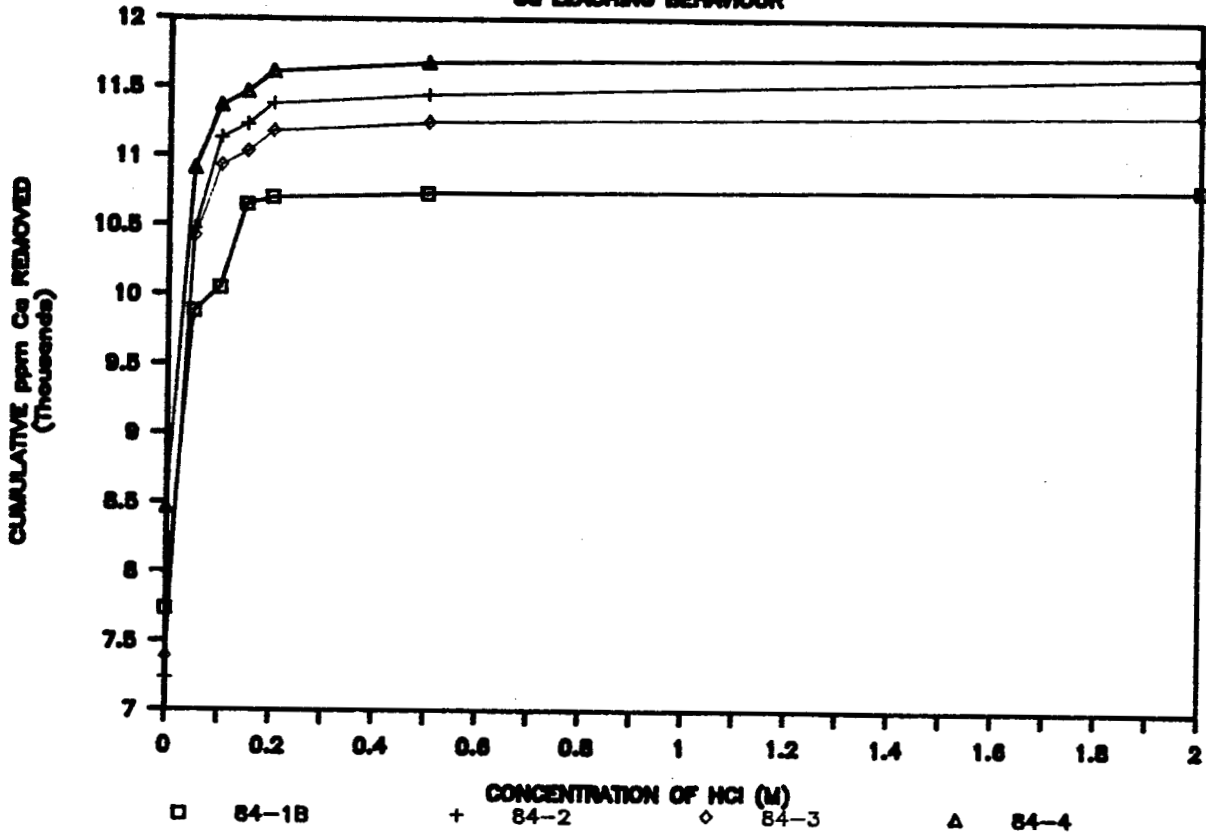
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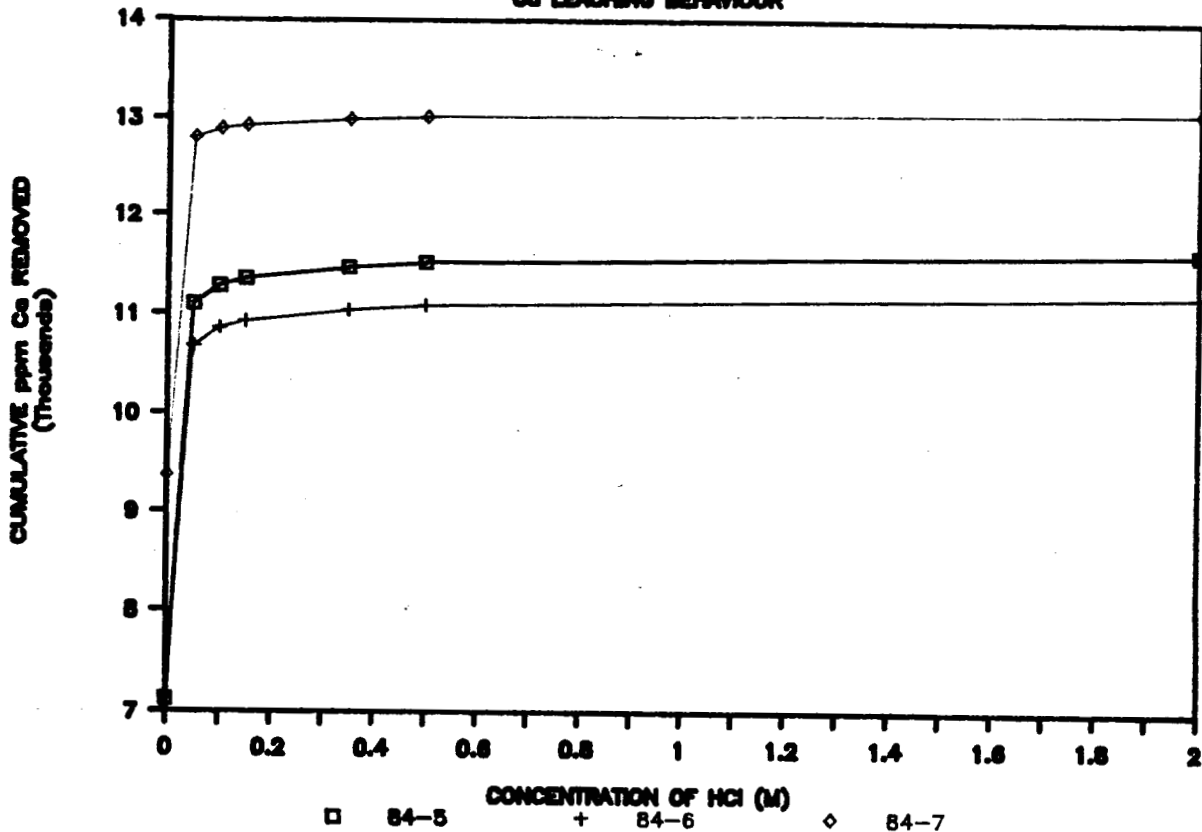


Figure 28. Cumulative removal of Ca from silica prepared by the addition of $KAl(SO_4)_2$ as a function of HCl concentration.

FI-84-8: 5.0 X 10E-4 M Al
FI-85-1: 4.0 X 10E-4 M Al

Figure 29. Cumulative removal of Ca from silica prepared by the addition of $KAl(SO_4)_2$ as a function of HCl concentration.

a. FI-85-2A: 2.5 X 10E-4 M Al
FI-85-2B: 2.0 X 10E-4 M Al
FI-85-2D: 1.0 X 10E-4 M Al

b. FI-85-2: 3.0 X 10E-4 M Al
FI-85-2C: 1.5 X 10E-4 M Al

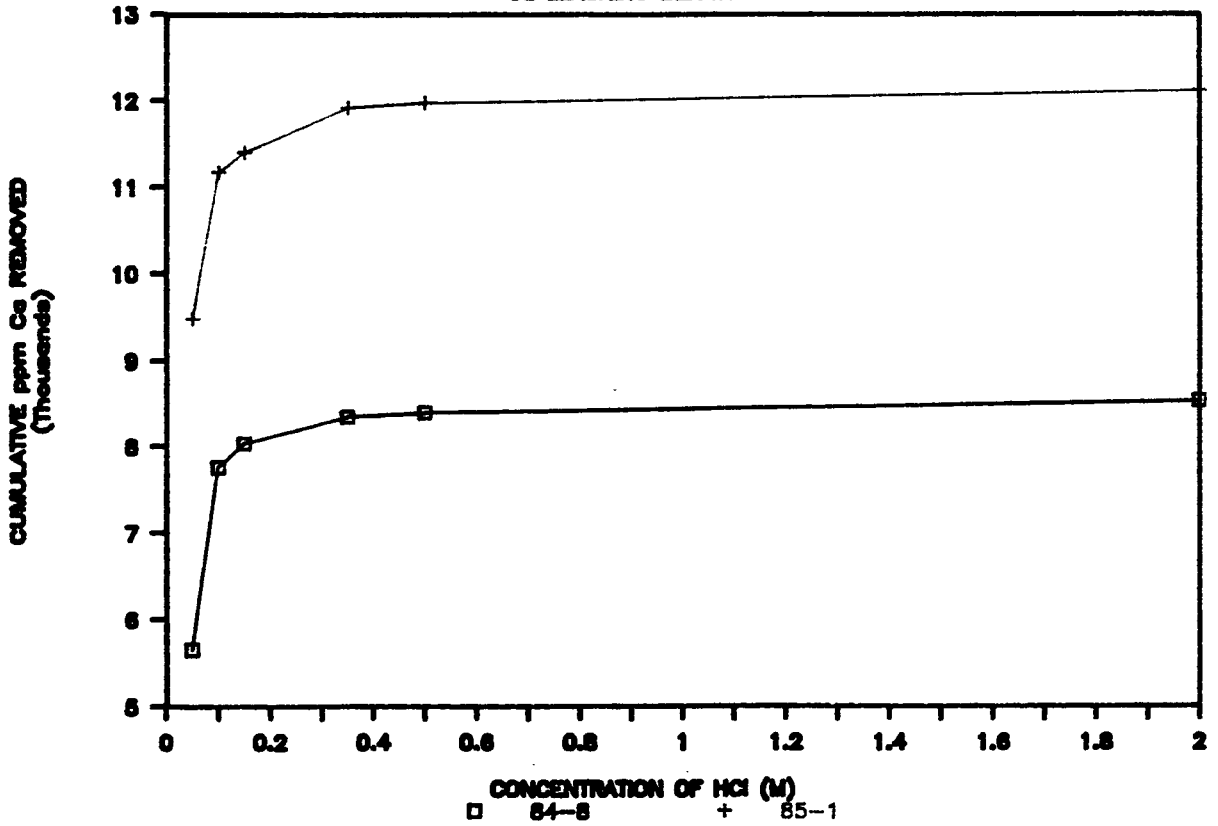
Figure 30: Cumulative removal of Ca from silica prepared by the addition of $Al_2(SO_4)_3$ as a function of HCl concentration.

a. FI-85-3: 5.0 X 10E-4 M Al
FI-85-4: 4.0 X 10E-4 M Al
FI-85-5: 3.0 x 10E-4 M Al
FI-85-6: 2.5 X 10E-4 M Al

b. FI-85-7: 2.0 X 10E-4 M Al
FI-85-8: 1.5 X 10E-4 M Al
FI-85-9: 1.0 X 10E-4 M Al

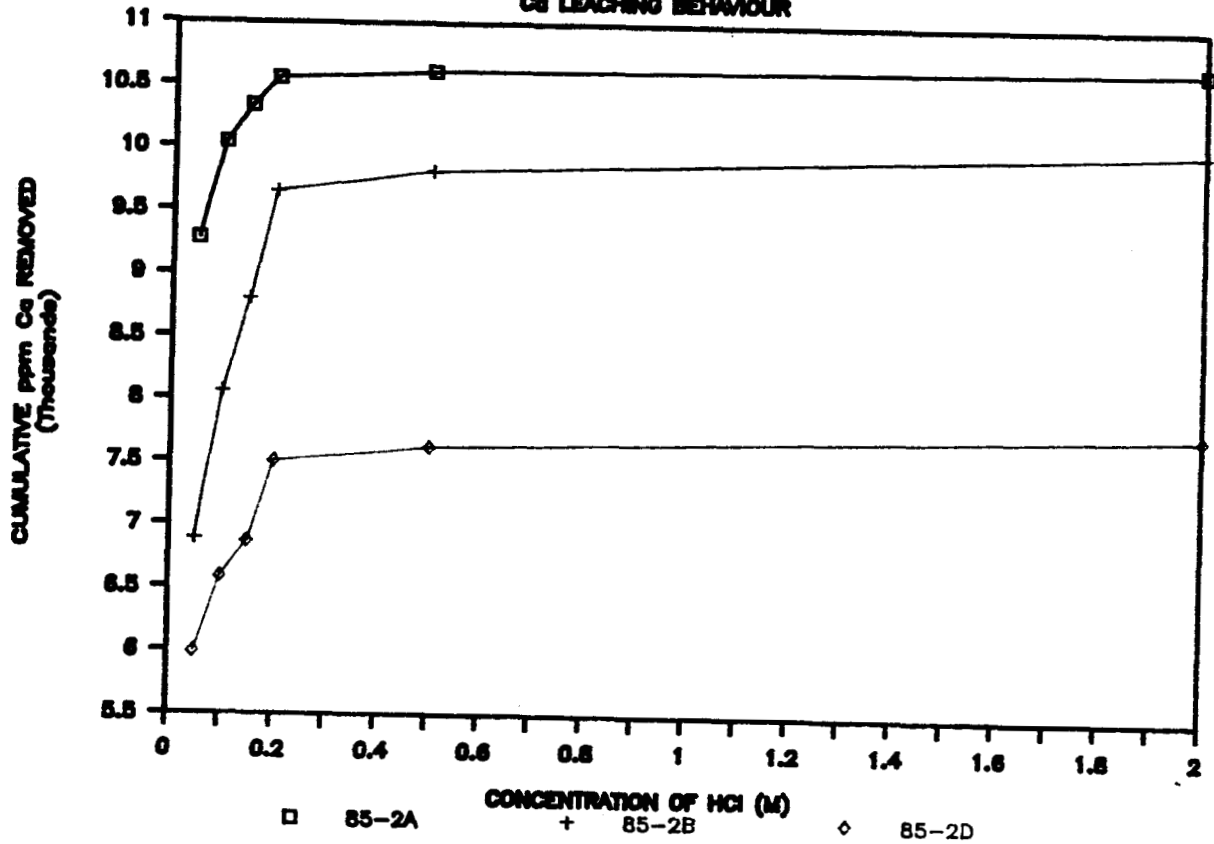
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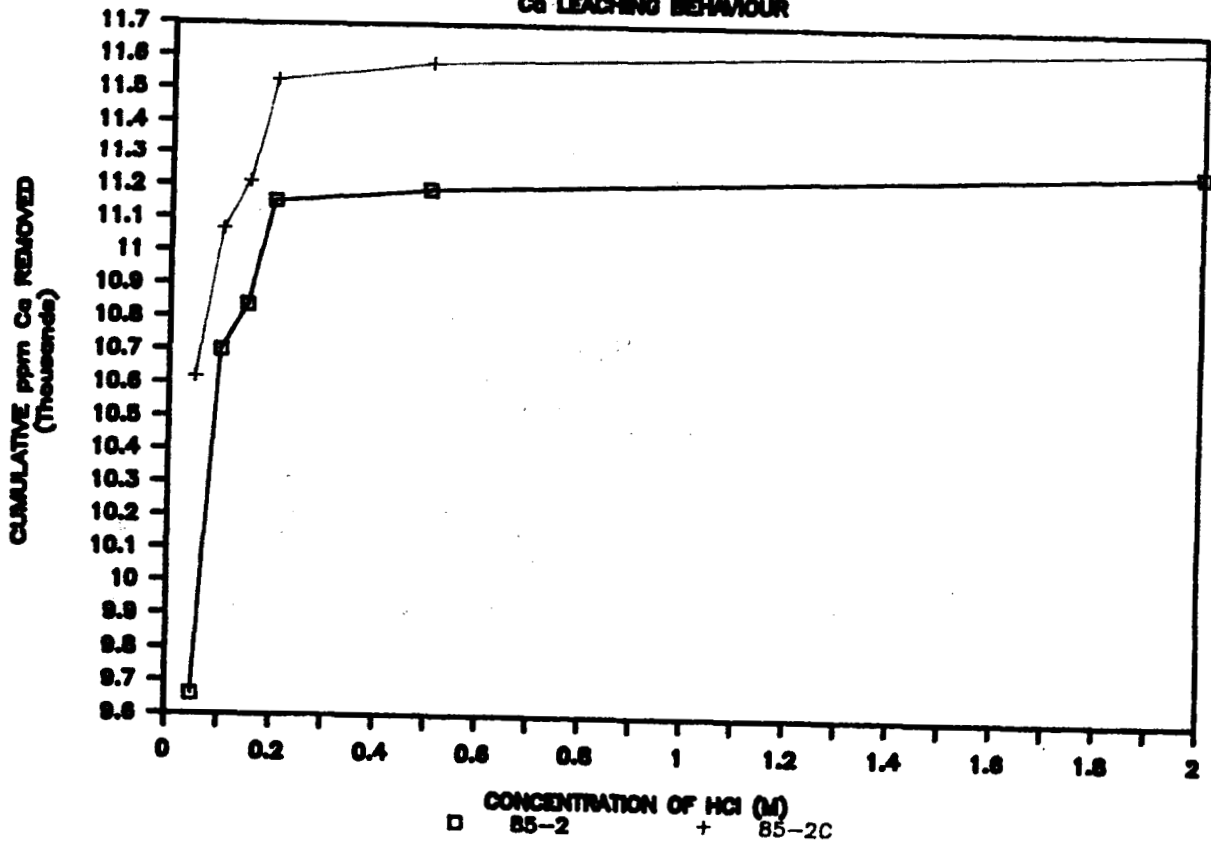
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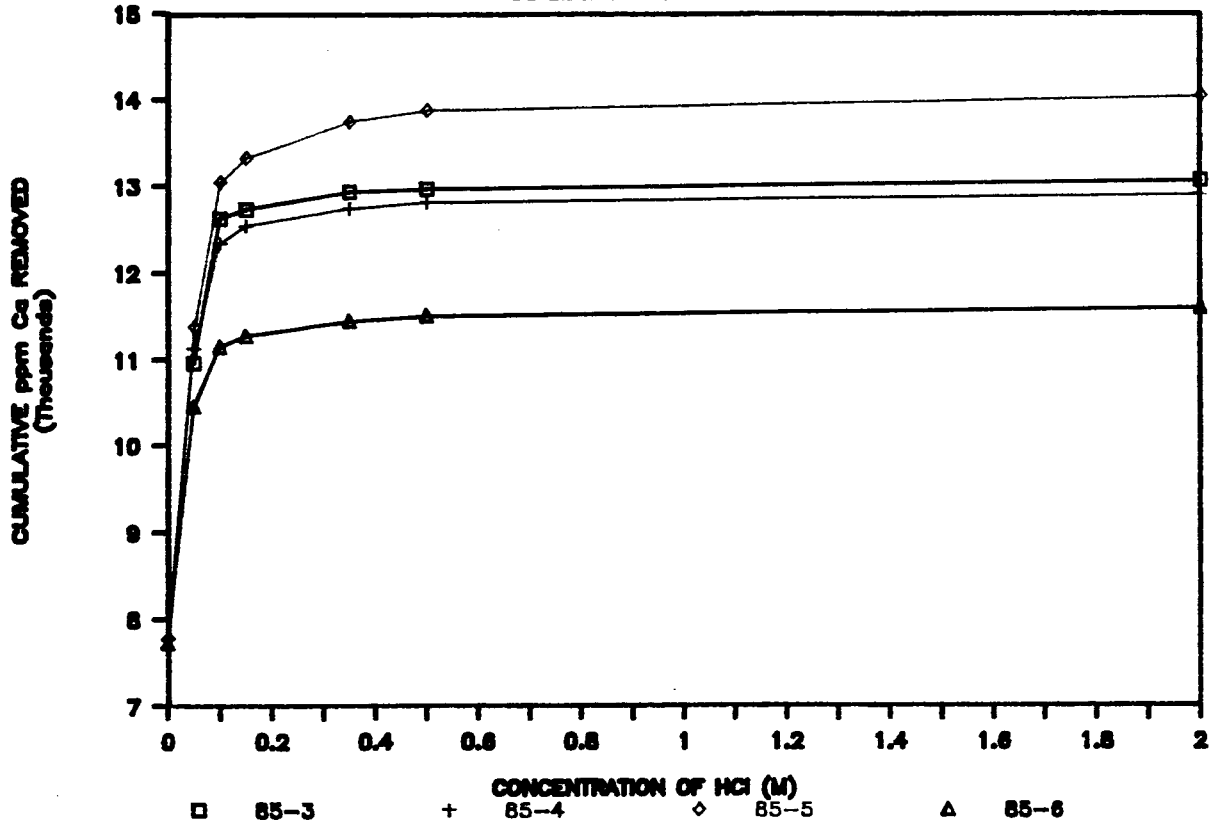
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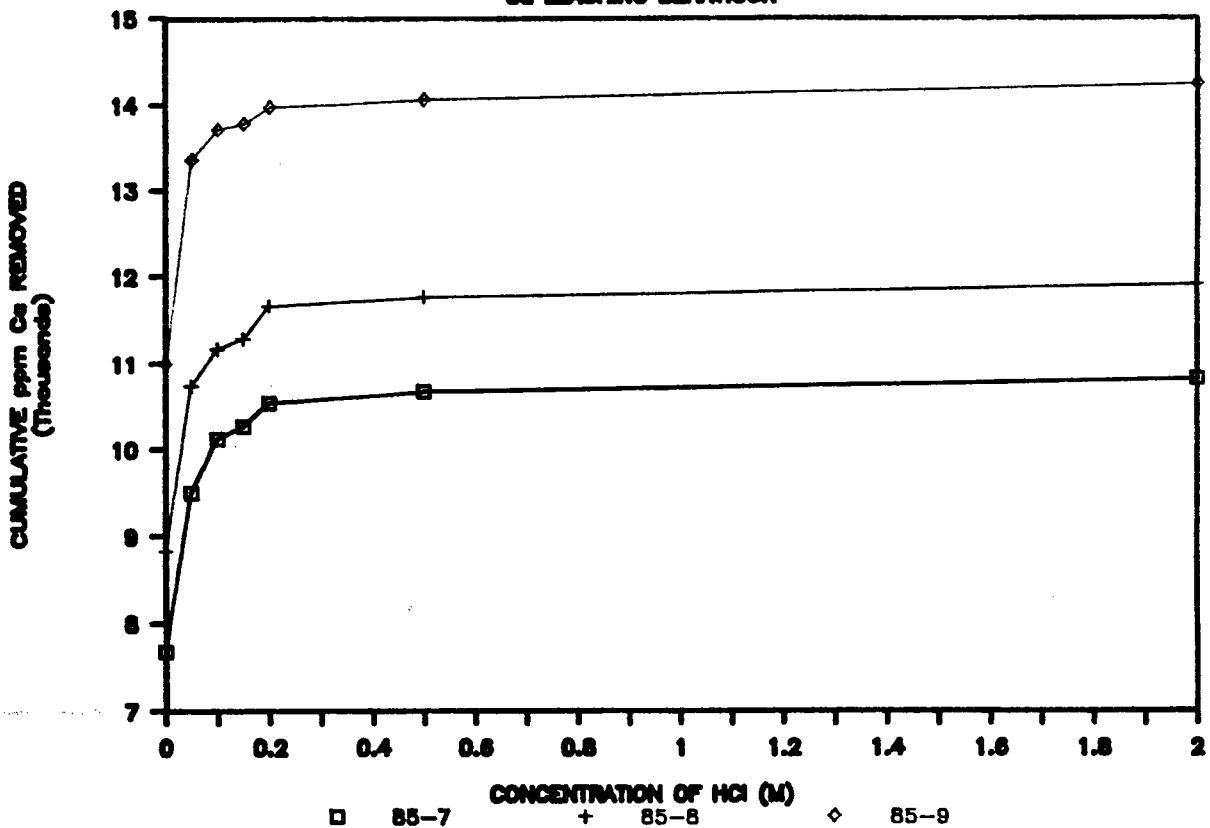
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those presented in Figure 26 for sample FI-90-1. The different amounts of Ca in the samples treated at HIG may result from three factors: 1) Larger volumes of HCl were employed at HGP-A for the leaching (50 mL versus 20 mL at HIG) and the lower concentration of Ca in on-site leached samples is a reflection of larger numbers of hydrogen ions present in solution to exchange with Ca. 2) The samples leached at HGP-A comprised an aqueous slurry from which metal ions adsorbed on or entrapped in the silica precipitates were readily removed due to the ease of interaction between the HCl and the suspended silica. 3) There may be ageing effects; as the silica ages it may increase ordering within its structure after which incorporated metals will be more difficult to remove. The slow (relative to acid concentration) release of Ca in these samples provides evidence in support of the last hypothesis. The removal curves shown in Figure 26 although asymptotic in shape indicate that a significant concentration of HCl (near 0.5 M) is necessary to leach out the Ca from the samples whereas at HGP-A only 0.146 M HCl was necessary to remove essentially all the Ca leachable with concentration of 2.0 M HCl (see Figures 4 and 5). Whether there is a significant difference in the lability of Ca when using 0.15 M versus 0.35 M to 0.5 M HCl is not certain and the difference may then be rather artificial. A number of samples were also subjected to leaching with slightly more concentrated HCl than the normal scheme presented in the experimental section of the report. We believe that the differences observed may not be of great importance. A discussion of this matter is included in the section dealing with the unrinsed samples. Since all samples which were brought back to HIG were dried at 110 degrees C, it is possible that some thermally induced restructuring of the silica may have occurred during the drying of the samples and affected their properties (Sharma, pers. comm., 1986). The increased ordering mentioned above for samples precipitated under natural conditions leads to a slight degree of crystallinity of the silica towards cristobalite, and results in an environment from which leaching of metal ions is more difficult than for completely amorphous silica.

Samples which were not rinsed with water on-site, were oven dried at HIG, and then subjected to leaching exhibit a slightly different behaviour than those described in the former paragraph. All the cumulative removal curves are also asymptotic but the asymptote is generally reached by the 0.15 M or 0.20 M leaching step. In several instances where 0.35 M HCl was employed in place of 0.20 M HCl the leveling off occurs at the former value whereas in others it occurs at the latter. This seems to indicate that there is a real difference between the samples in terms of leaching behaviour. Of additional interest is the fact that in all cases except where the sample was formed by the largest or the smallest addition of flocculating agent, the amount of Ca remaining after the series of leachings is much larger than that present in samples which were leached on-site at HGP-A. Such a behaviour again supports the hypothesis proposed regarding restructuring of the silica upon heating. The samples with low remanent Ca concentrations after leaching resemble those of the on-site leachings more than other samples from the same series. In all cases of samples prepared by enhanced precipitation, the majority of the Ca is labile and most likely not involved in structural sites. The majority of the Ca, present as small divalent cations, is probably adsorbed at the electrical double layer of the silica or physically entrapped and is thus easily replaced by hydrogen ions during leaching. Figures 27 through 30 show the cumulative removal curves discussed above. Any additional Ca which is not easily leached by up to 2.0 M HCl could then be involved in some structural arrangements. Considering the data presented in Figures 1 through 3 and in Table 1 where we show that the Ca concentration in the silica prior to leaching drops significantly with the highest addition of Fe or Alum, there may be a relationship between the flocculating cations Fe or Al which are proposed to act in a bridging capacity and Ca which may play a similar role within the silica

structure. The increased concentration of Fe and Al, however, may simply lead to a displacement of divalent Ca from the surface of the silica as a result of preferential electrostatic or specific adsorption of the former species. Residual concentrations of Ca in the silica support this contention since for the samples in question the remaining concentration of Ca is lower than for other samples in the same series.

The Ca leaching behaviour for sample X-29-1 is considerably different from those discussed in the previous paragraphs. Examination of the data in Table 2 and the cumulative removal of Ca presented in Table 7 reveals that only 28.2% of the original Ca concentration is removed by the serial leaching process. The amount is considerably less than the 60% to 94% removed from the samples discussed above. The striking difference is however explainable even though both trivalent metal ion and NaOH enhanced flocculations result in the rapid formation of silica precipitates which would be expected to only weakly bind other metal ions. Sample X-29-1 in spite of its rapid formation above pH 9 is a mixture of crystalline aragonite (calcium carbonate) and tilleyite (calcium silicate carbonate) both of which have a well ordered structure (Deer et al., 1980). The removal curve displayed in Figure 31 appears to exhibit two separate episodes of Ca removal. The first occurs below 0.2 M HCl and the second above 0.35 M HCl. The presence of the two aforementioned minerals is consistent with the observed Ca removal curve as aragonite is more soluble in dilute HCl than tilleyite. It is probable that the Ca leached with HCl <0.2 M is from the aragonite whereas that leached with 0.35 M to 2.0 M HCl is derived from the partial dissolution of tilleyite. Deer et al. (1980) indicate that tilleyite is composed of discrete Si₂O₇ and CO₃ groups linked by Ca atoms. The fact that only 28 % of the Ca is removed may result from preferential attack of the CO₃ linked Ca leaving behind a very poorly crystalline to nearly amorphous calcium silicate (Mackenzie, pers. comm. 1986).

In Figure 32 we present the removal curves for Ca in natural silica scale and in precipitates from unflushed brine. It is immediately apparent that the removal of Ca from X-29-2, which formed by deposition in the atmospheric flash tank is relatively difficult and increases with increased HCl concentration. Only approximately 15% of the amount of Ca in this sample is leached out. The behaviour exhibited is indicative of Ca which has been strongly bound by the silica during the slow depositional process and is involved in more than electrostatic adsorption at the silica surface. In samples X-29-4 and 29-5 where the concentration of Ca prior to leaching is very similar (see Table 2), there appears to be a significant difference in the availability of the Ca upon HCl attack. The former sample exhibits a slightly lower removal efficiency than does the latter. The adsorption of divalent Ca on the silica may be different during precipitation in the presence of Fe instead of Al hydroxy complexes. The sample prepared in the presence of Fe thus releases less Ca possibly due to interactions between divalent Ca cations and negatively charged Fe hydroxy-complexes, whereas in the sample prepared in the presence of Al there are no such interactions as the iep of the Al hydroxide in the silica has not been exceeded. The leaching behaviour exhibited by sample X-29-3 is consistent with its slow mode of formation at the turbine nozzle inlet. Nearly one third of the Ca is released when leaching with up to 2.0 M HCl and most of that is released during the very dilute HCl steps since it is held to the silica surface by electrostatic adsorptive forces. The remainder of the Ca in the sample though is tightly bound and not readily released by the HCl solutions employed in our experiments.

Magnesium:

The concentration of Mg in the geothermal brine is very low as compared to normal seawater or a nearly 50 % mixture of seawater and meteoric water as

Figure 31. Cumulative removal of Ca from silica deposited by the addition of NaOH to spent brine, pH > 9.08.

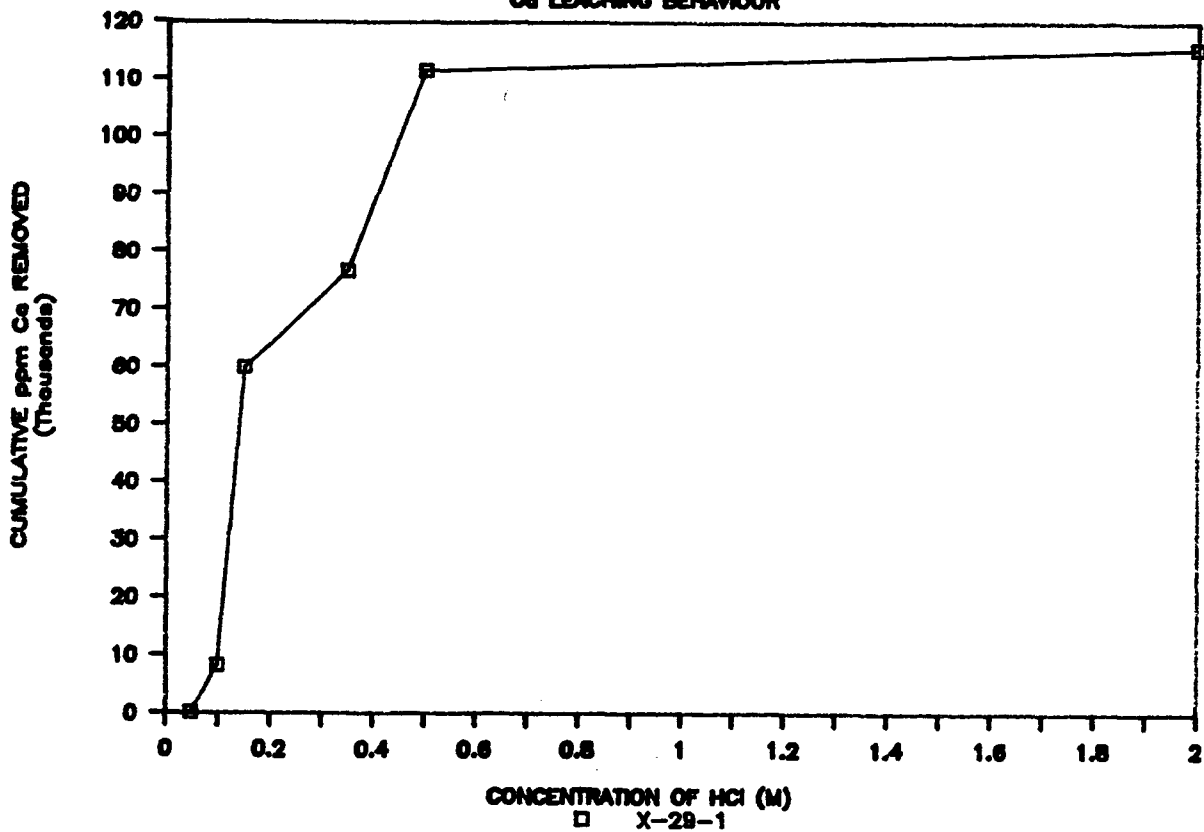
Figure 32. Cumulative removal of Ca from silica precipitation from HGP-A.

- a. X-29-3: silica scale deposit from turbine nozzle inlet.
- X-29-4: silica precipitated by addition of 2.5×10^{-4} M Fe(III) to unflashed brine at pH = 8.0
- X-29-5: silica precipitated by addition of 2.5×10^{-4} M Al to unflashed brine at pH = 8.0

- b. X-29-2: silica deposited by natural precipitation in spent brine pH ~7.5

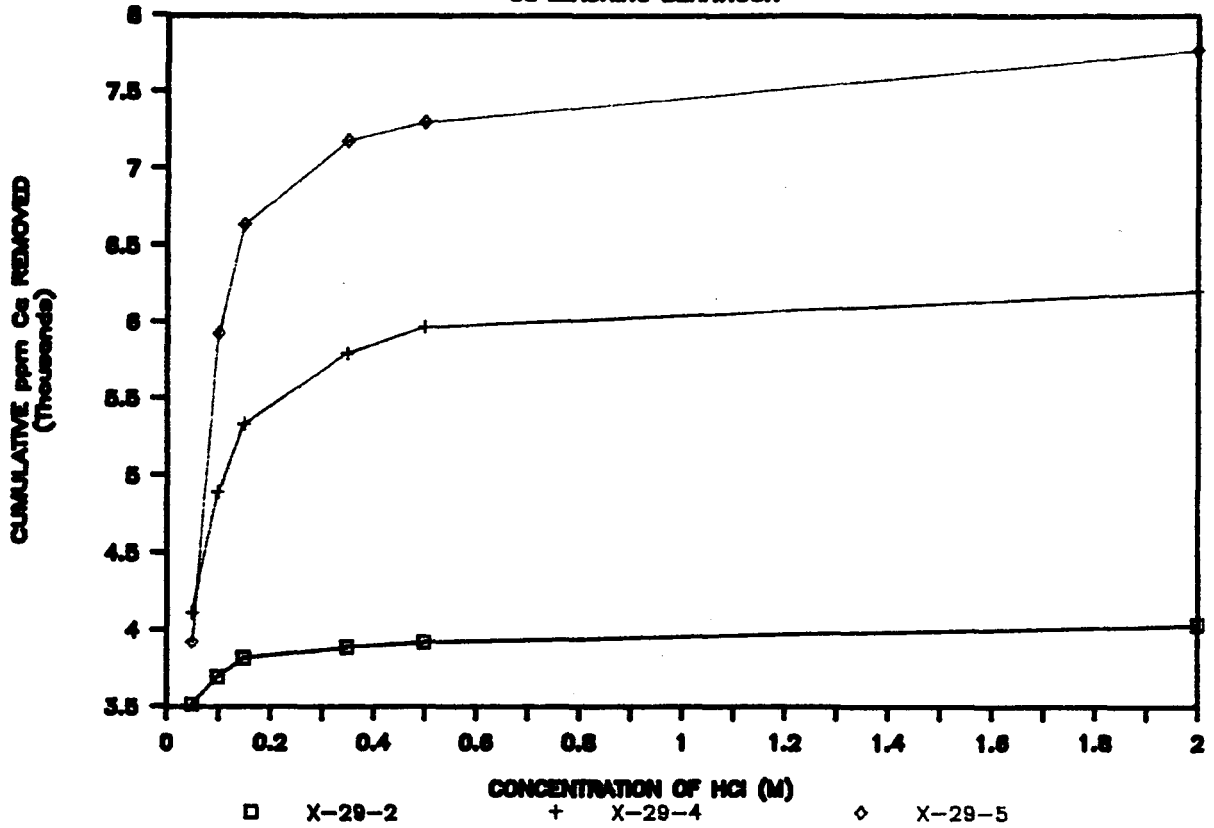
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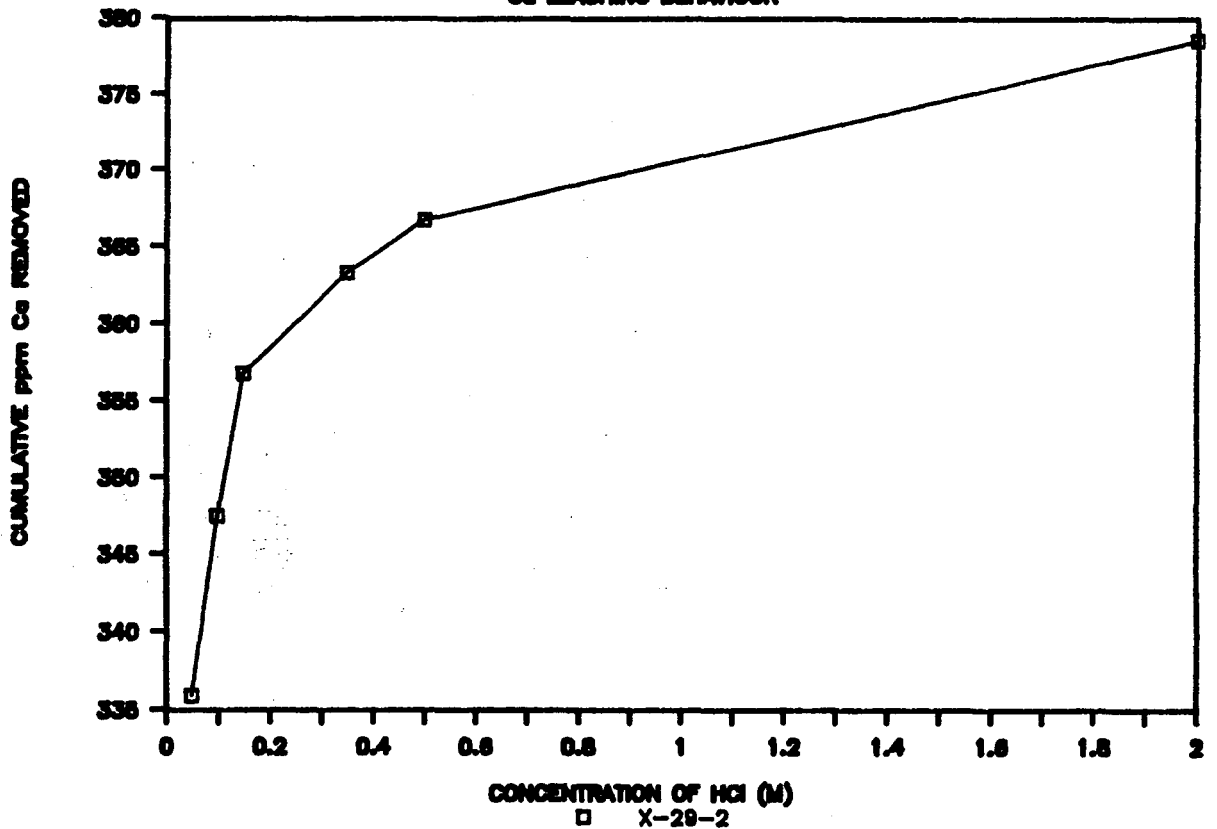


TABLE 9

CUMULATIVE REMOVAL OF Mg FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.20	0.50	2.00
	Concentration of Mg (in ppm)						
FI-84-1B	10.30	7.10	1.20	1.10	0.60	0.30	0.60
cum.	10.30	17.40	18.60	19.70	20.30	20.60	21.20
FI-84-2	3.90	5.40	2.20	0.80	0.90	0.60	1.30
cum.	3.90	9.30	11.50	12.30	13.20	13.80	15.10
FI-84-3	3.90	4.70	2.00	0.90	0.90	0.50	0.80
cum.	3.90	8.60	10.60	11.50	12.40	12.90	13.70
FI-84-4	5.50	3.50	1.90	0.80	0.80	0.40	0.50
cum.	5.50	9.00	10.90	11.70	12.50	12.90	13.40
FI-84-5	5.90	5.80	0.90	0.70	0.70	0.30	1.00
cum.	5.90	11.70	12.60	13.30	14.00	14.30	15.30
FI-84-6	4.70	5.20	0.90	0.60	0.70	0.50	1.30
cum.	4.70	9.90	10.80	11.40	12.10	12.60	13.90
FI-84-7	5.10	4.60	0.40	0.40	0.70	0.40	1.10
cum.	5.10	9.70	10.10	10.50	11.20	11.60	12.70
FI-84-8		4.30	2.60	0.20	0.90	0.00	1.70
cum.		4.30	6.90	7.10	8.00	8.00	9.70
FI-85-1		4.30	2.30	0.20	1.00	0.00	1.40
cum.		4.30	6.60	6.80	7.80	7.80	9.20
FI-85-2		3.60	1.20	0.00	0.30	0.00	0.10
cum.		3.60	4.80	4.80	5.10	5.10	5.20
FI-85-2A		3.20	0.60	0.90	0.20	0.00	0.00
cum.		3.20	3.80	4.70	4.90	4.90	4.90
FI-85-2B		2.60	0.70	0.60	0.90	0.20	0.50
cum.		2.60	3.30	3.90	4.80	5.00	5.50
FI-85-2C		3.10	0.30	0.10	0.60	0.00	0.00
cum.		3.10	3.40	3.50	4.10	4.10	4.10
FI-85-2D		2.50	1.00	0.80	1.10	0.80	0.80
cum.		2.50	3.50	4.30	5.40	6.20	7.00
FI-85-3		6.10	4.40	0.60	1.20	0.40	2.10
cum.		6.10	10.50	11.10	12.30	12.70	14.80
FI-85-4	3.10	4.10	2.40	0.80	1.20	0.50	0.90
cum.	3.10	7.20	9.60	10.40	11.60	12.10	13.00

TABLE 9

CUMULATIVE REMOVAL OF Mg FROM SILICA AS A FUNCTION OF ACID CONCENTRATION

SAMPLE	Molarity of HCl						
	0.00	0.05	0.10	0.15	0.20	0.50	2.00
	Concentration of Mg (in ppm)						
FI-85-5	3.90	4.00	3.50	1.10	2.60	1.00	1.80
cum.	3.90	7.90	11.40	12.50	15.10	16.10	17.90
FI-85-6	3.10	3.50	1.90	0.70	12.00	0.50	1.60
cum.	3.10	6.60	8.50	9.20	21.20	21.70	23.30
FI-85-7	3.50	1.70	0.80	0.20	0.60	0.40	0.70
cum.	3.50	5.20	6.00	6.20	6.80	7.20	7.90
FI-85-8	4.90	1.90	0.60	0.30	1.00	0.30	1.20
cum.	4.90	6.80	7.40	7.70	8.70	9.00	10.20
FI-85-9	4.90	1.80	0.40	0.10	0.30	0.10	0.40
cum.	4.90	6.70	7.10	7.20	7.50	7.60	8.00
FI-90-1		6.40	2.10	0.80	1.00	4.40	2.20
cum.		6.40	8.50	9.30	10.30	14.70	16.90
FI-93-1		2.30	1.65	1.40	14.35	6.10	7.65
cum.		2.30	3.95	5.35	19.70	25.80	33.45
FI-94-2		3.90	1.70	0.40	0.70	0.60	2.10
cum.		3.90	5.60	6.00	6.70	7.30	9.40
FI-95-1		3.50	3.00	1.60	5.50	2.80	4.20
cum.		3.50	6.50	8.10	13.60	16.40	20.60
X-29-1		0.30	1.30	32.20	9.40	11.00	2.20
cum.		0.30	1.60	33.80	43.20	54.20	56.40
X-29-2		16.00	1.10	2.08	2.68	0.70	7.64
cum.		16.00	17.10	19.18	21.86	22.56	30.20
X-29-3		56.50	49.00	112.50	60.50	44.00	157.00
cum.		56.50	105.50	218.00	278.50	322.50	479.50
X-29-4		13.20	3.60	3.23	4.00	2.14	2.96
cum.		13.20	16.80	20.03	24.03	26.17	29.13
X-29-5		22.10	5.44	4.08	4.12	1.16	6.07
cum.		22.10	27.54	31.62	35.74	36.90	42.97

is encountered at HGP-A (De Carlo and Thomas, 1985). The main mechanism which removes Mg from the geothermal fluids (or seawater) during high temperature hydrothermal reactions is the formation of the alteration mineral chlorite; this process results in a nearly complete uptake of any Mg that is present in the fluids (Mottl 1983, Thompson 1983). As a result it is expected that very little Mg is available for incorporation into silica formed from geothermal brine. The data presented in Tables 1 and 2 are generally in agreement with previous observations; the samples formed by rapid precipitation all contain less than 60 ug/g Mg, and the two scale samples which formed by natural deposition in the flash tank and in the turbine nozzle inlet contain 93 and 1385 ug/g respectively. The higher concentration in the scales is expected as both deposits accumulated over extended periods allowing for a greater extent of scavenging by the silica surface. Preferential adsorption of Mg over Ca at the silica water interface under otherwise identical conditions is also to be expected due to the higher charge to size ratio exhibited by Mg (Huheey 1978, Parks 1967).

In light of the above it would be expected that very little Mg should be leached from the precipitated silica and the scale deposits from HGP-A. The data presented in Table 9 support this contention for all samples studied. There is, however, a significant difference in the release of Mg from the silica samples formed by various processes. Generally, the samples which were precipitated by the addition of Fe(III) contain two to three times as much Mg as those precipitated by the addition of Al (alum or aluminum sulfate). The preferential incorporation of Mg onto Fe-rich silica is likely to be related to more favorable negative surface charges encountered on this type of silica. Essentially all the Mg present in the samples is leached out with less than 0.5 M HCl as can be seen by comparing the data from Table 1 and those shown in Figure 33. From these results it appears that Mg in rapidly formed silica is held to the surface principally by electrostatic attraction. The removal of Mg from samples prepared by addition of Al to the brine is also nearly quantitative with most of the Mg removed by less than 0.5 M HCl. The slightly different shape of the removal curves presented in Figures 34 and 35 as well as the slight discrepancies in the actual amount of Mg leached relative to that which was originally present in the samples is believed to be an artifact of the analysis. The extremely low concentrations of Mg in the solutions analyzed lead to a large degree of uncertainty in the results; this is readily seen by the large standard deviations of the analyses presented in Table 1. The only conclusive results of these experiments are a lesser incorporation of Mg into the silica precipitated by the addition of Al as a result of less optimum surface charge characteristics than in the case of the Fe-rich silica, and a nearly complete removal of electrostatically adsorbed Mg from the silica upon leaching with dilute HCl.

Samples which were rinsed after precipitation at HGP-A exhibit a removal behaviour which is indicative of the nature of the forces holding the Mg at the silica surface. The plots presented in Figure 36 show a more gradual release of the Mg than those in Figures 33 through 35. It appears that very little Mg was removed by the rinsing process at HGP-A (see Table 1). It is quite unfortunate that in these analyses as in those presented in the previous paragraph we were pushing the limit of detection of the instrument because this precludes firm conclusions as to the surface behaviour of Mg on silica. Nonetheless, we believe that the gradual release from the samples indicates an electrostatic attraction of Mg to the silica rather than entrapment of Mg from the brine itself. Why the curves are not identical to those of the unrinsed samples remains a puzzle.

The removal of Mg from silica precipitated by the addition of NaOH to the brine discharge in the atmospheric flash tank is presented in Figure 37a. Although the initial concentration of Mg in this sample was near 60 ug/g, only

Figure 33. Cumulative removal of Mg from silica prepared by the addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of HCl concentration.

- a. FI-84-1B: 5.0×10^{-4} M Fe(III)
FI-84-2: 4.0×10^{-4} M Fe(III)
FI-84-3: 3.0×10^{-4} M Fe(III)
FI-84-4: 2.5×10^{-4} M Fe(III)

- b. FI-84-5: 2.0×10^{-4} M Fe(III)
FI-84-6: 1.5×10^{-4} M Fe(III)
FI-84-7: 1.0×10^{-4} M Fe(III)

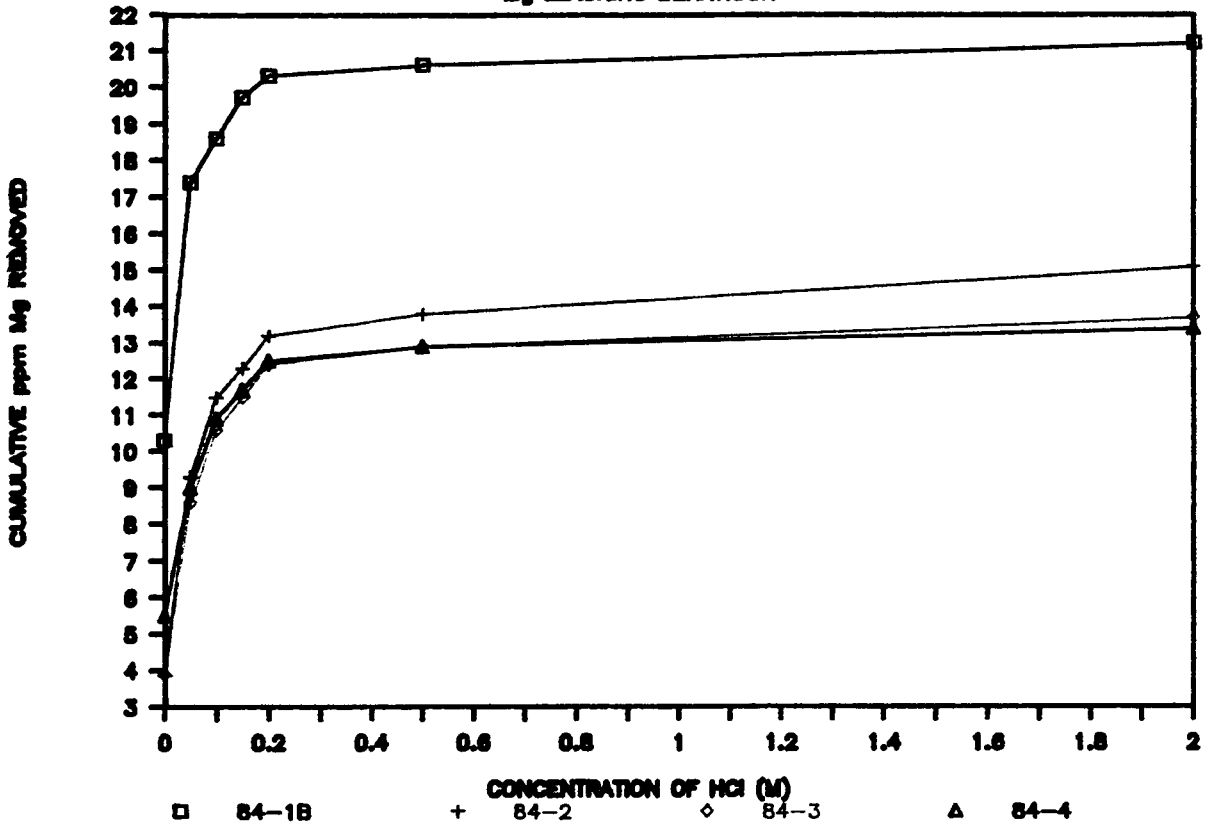
Figure 34. Cumulative removal of Mg from silica prepared by the addition of $\text{KAl}(\text{SO}_4)_2$ as a function of HCl concentration.

- a. FI-84-8: 5.0×10^{-4} M Al
FI-85-1: 4.0×10^{-4} M Al
FI-85-2D: 1.0×10^{-4} M Al

- b. FI-85-2: 3.0×10^{-4} M Al
FI-85-2A: 2.5×10^{-4} M Al
FI-85-2B: 2.0×10^{-4} M Al
FI-85-2C: 1.5×10^{-4} M Al

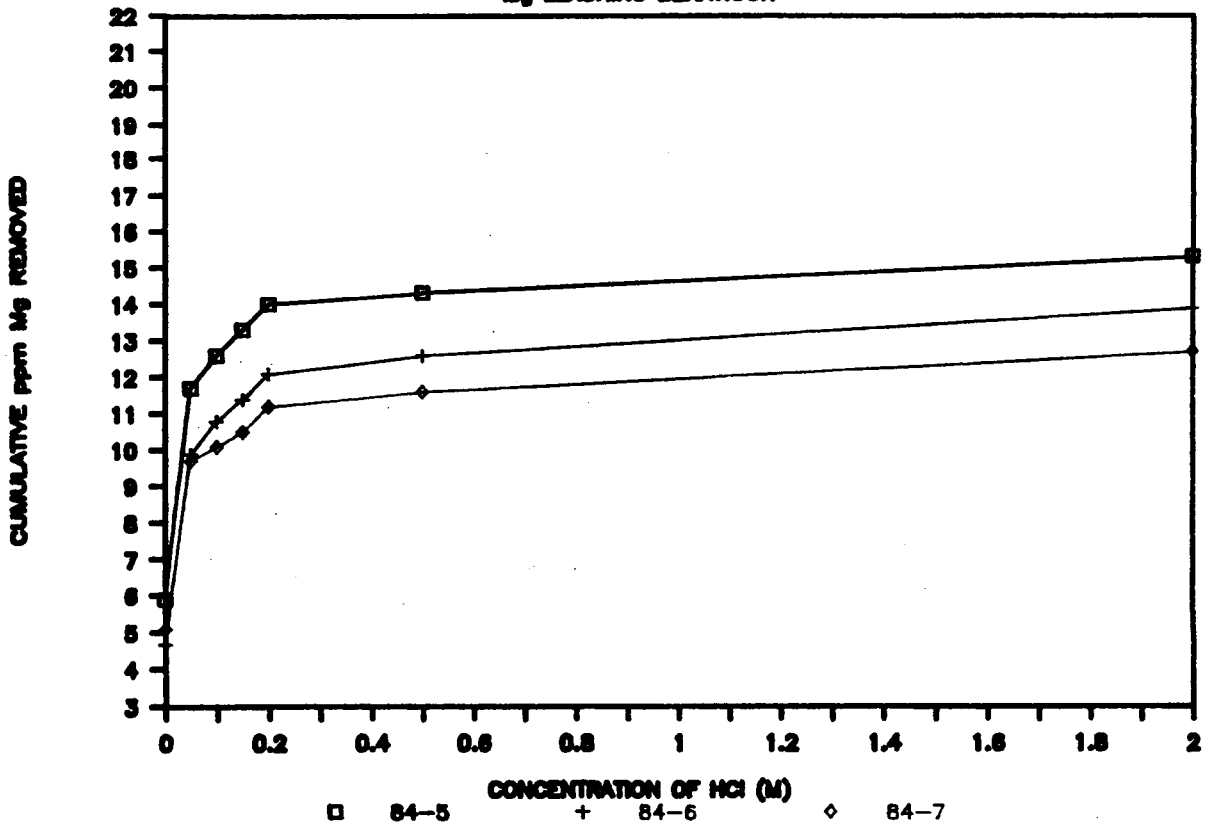
GEOTHERMAL SILICA PROJECT

Mg LEACHING BEHAVIOUR



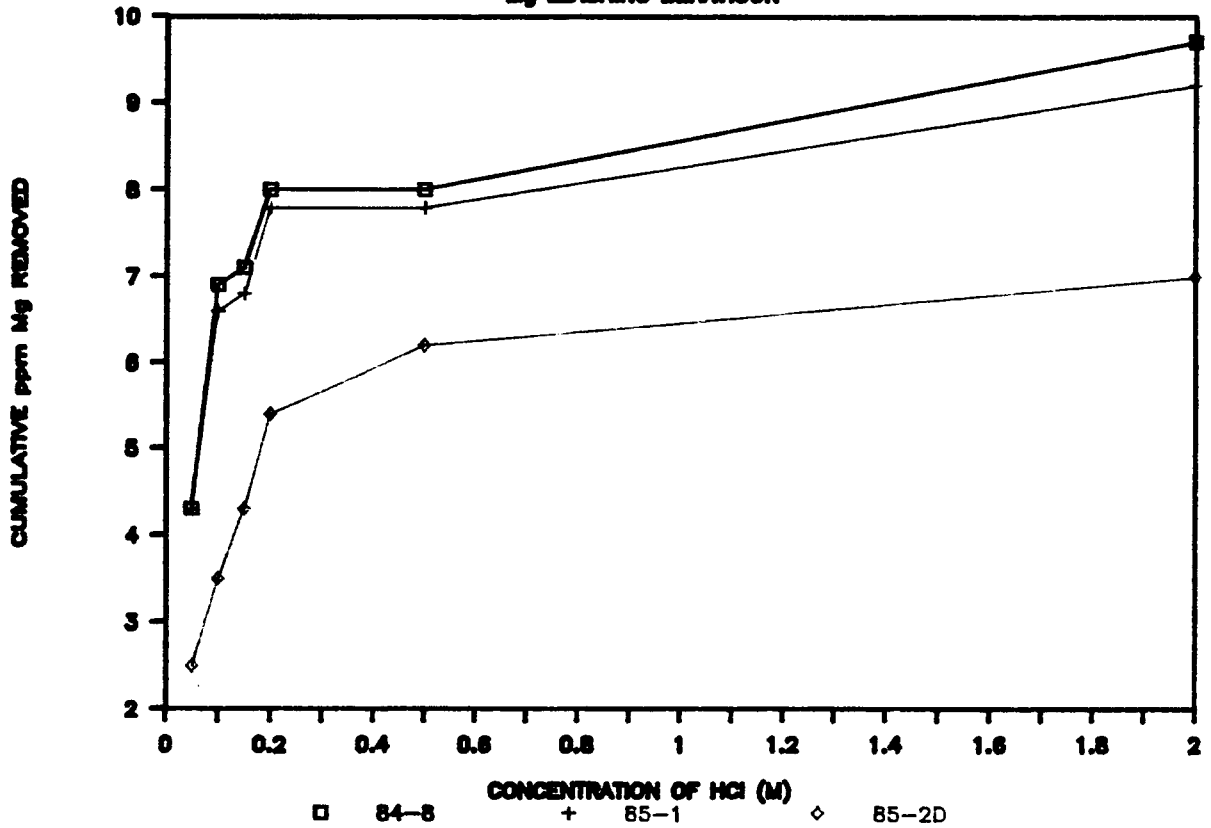
GEOTHERMAL SILICA PROJECT

Mg LEACHING BEHAVIOUR



GEOTHERMAL SILICA PROJECT

Mg LEACHING BEHAVIOUR



GEOTHERMAL SILICA PROJECT

Mg LEACHING BEHAVIOUR

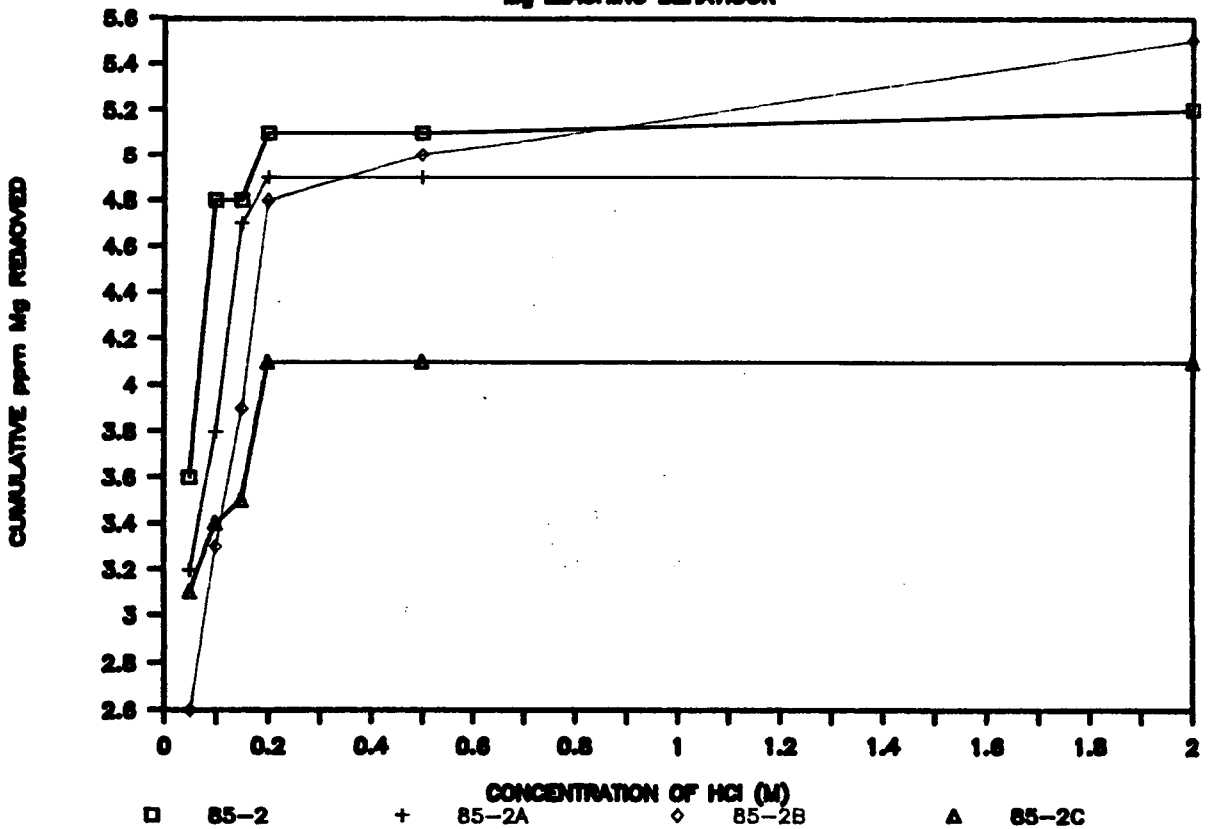


Figure 35. Cumulative removal of Mg from silica prepared by the addition of $\text{Al}_2(\text{SO}_4)_3$ as a function of HCl concentration.

- a. FI-85-7: 2.0×10^{-4} M Al
FI-85-8: 1.5×10^{-4} M Al
FI-85-9: 1.0×10^{-4} M Al

- b. FI-85-3: 5.0×10^{-4} M Al
FI-85-4: 4.0×10^{-4} M Al
FI-85-5: 3.0×10^{-4} M Al
FI-85-6: 2.5×10^{-4} M Al

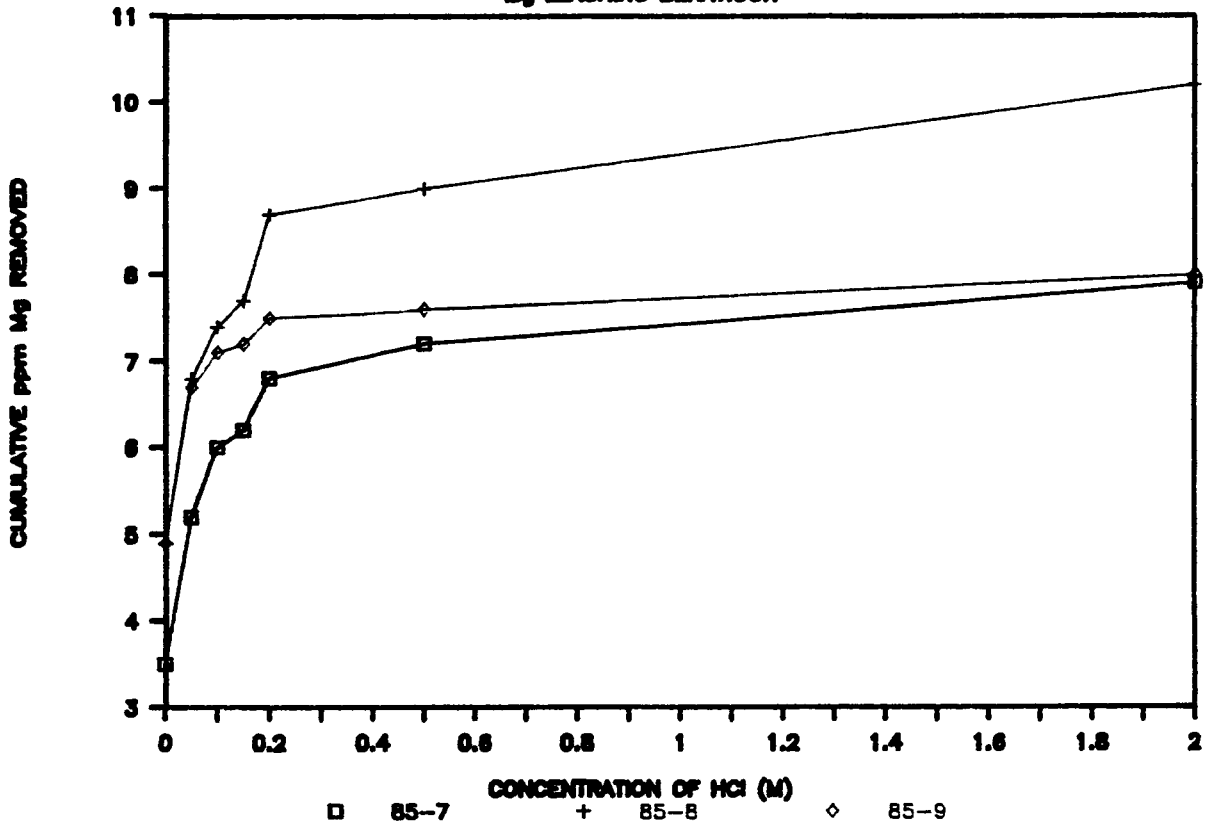
Figure 36. Cumulative removal of Mg from water rinsed silica prepared by the addition of $\text{Fe}_2(\text{SO}_4)_3$ as a function of the HCl concentration.

- a. FI-90-1: 1.25×10^{-4} M Fe(III), and rinsed with distilled deionized (d.d.)
FI-94-2: 2.5×10^{-4} M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant
FI-95-1: 1.5×10^{-4} M Fe(III), 37.5 mg/L lauryl ammonium chloride surfactant, and rinsed with d.d. H_2O

- b. FI-93-1: 2.5×10^{-4} M Fe(III), not rinsed

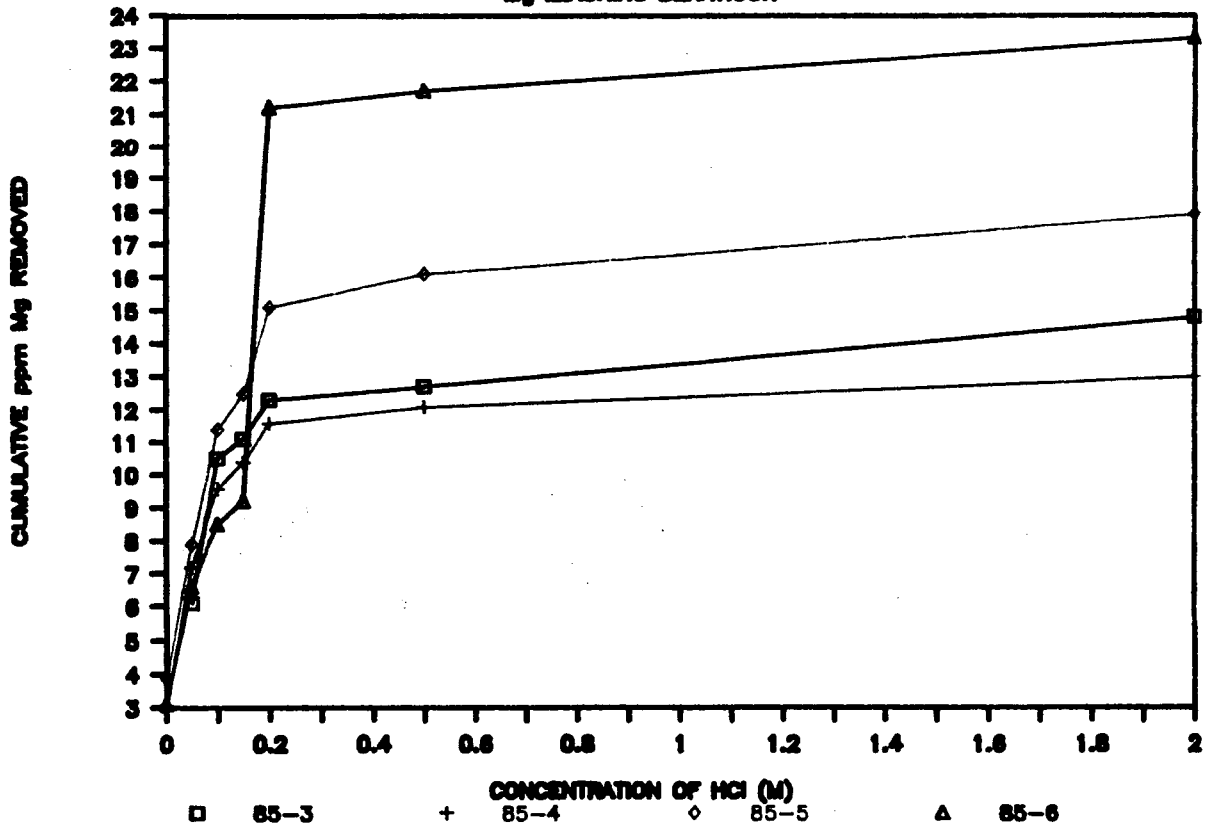
GEOTHERMAL SILICA PROJECT

Mg LEACHING BEHAVIOUR



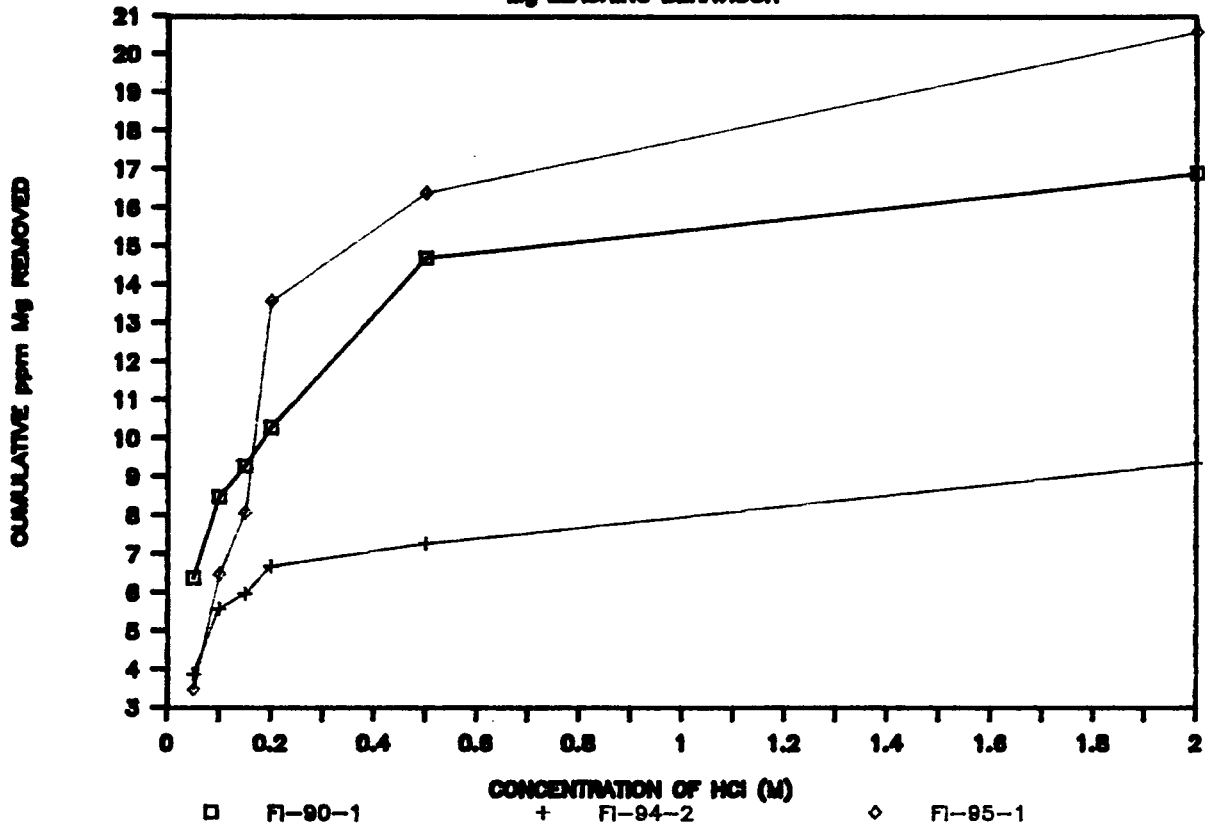
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Mg LEACHING BEHAVIOUR



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Mg LEACHING BEHAVIOUR



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Mg LEACHING BEHAVIOUR

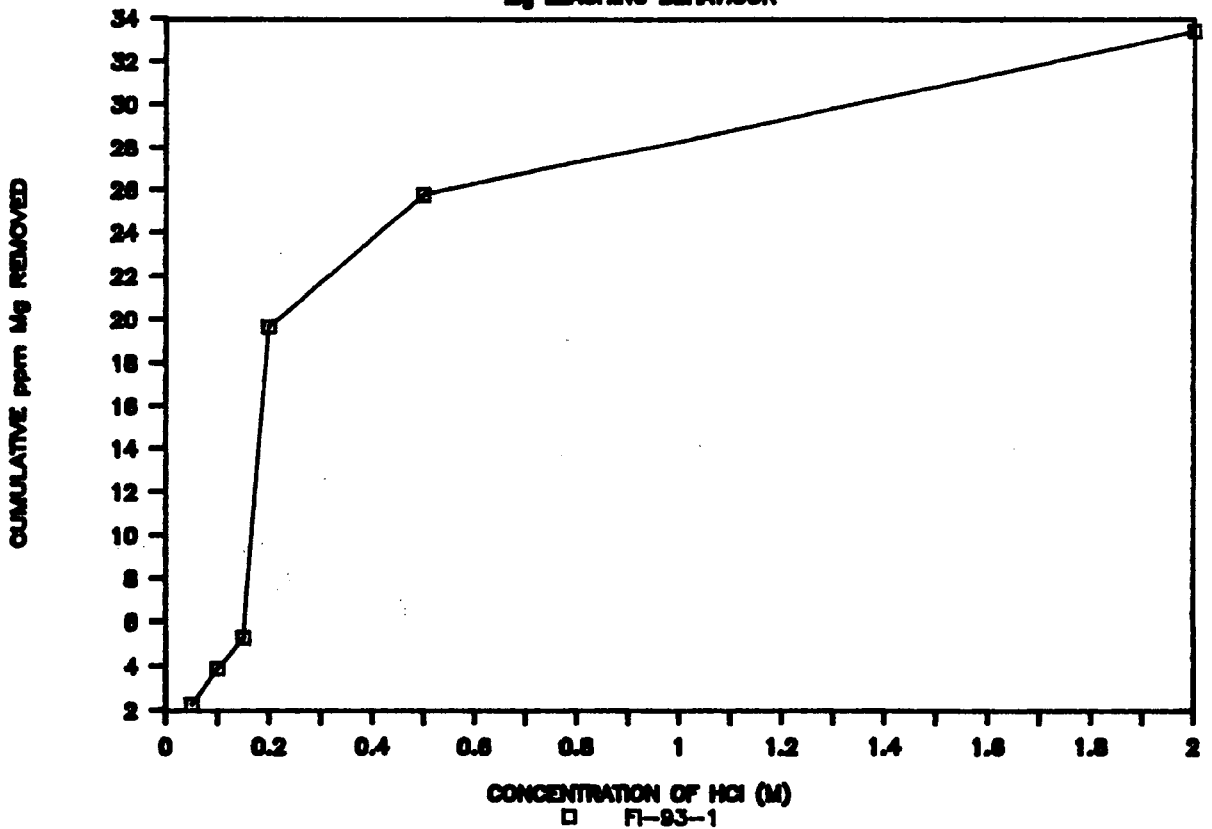


Figure 37. Cumulative removal of Mg from silica deposits from HGP=A as a function of the HCl concentration.

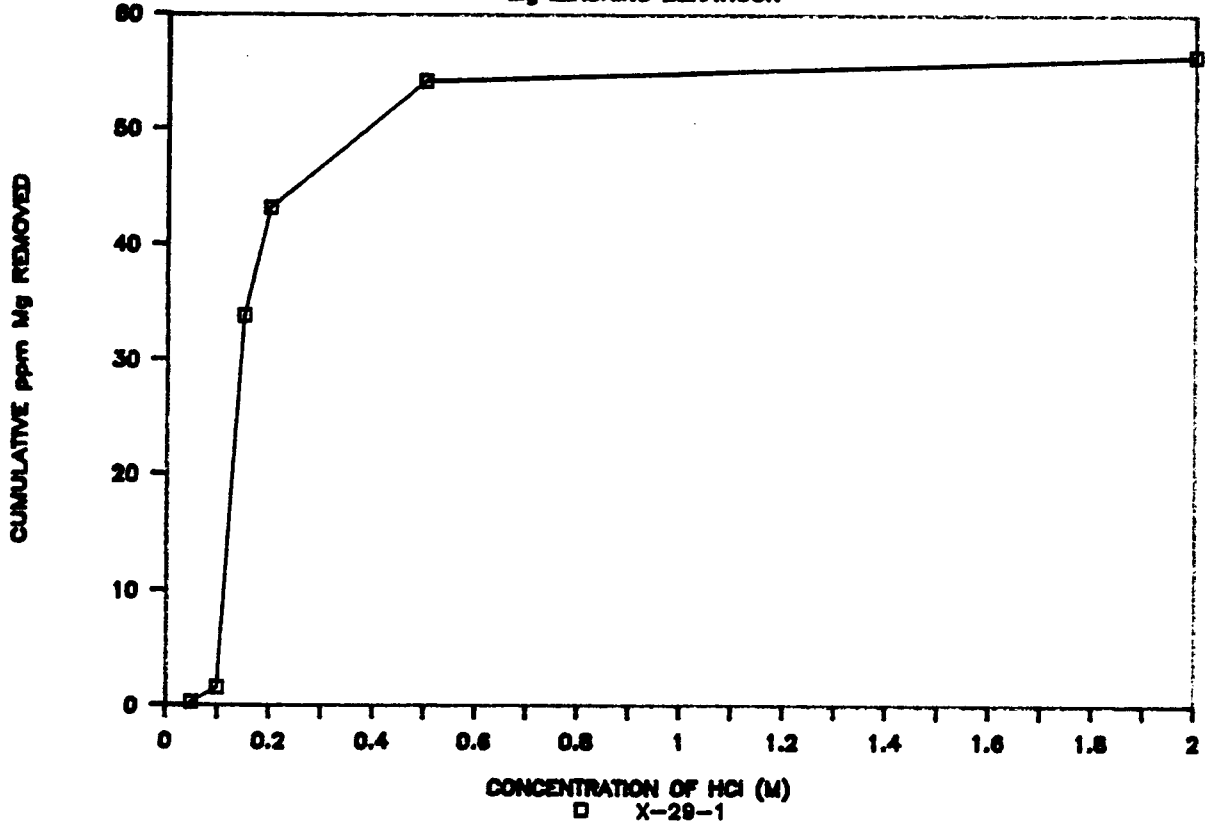
- a. X-29-2: silica deposited by natural precipitation in spent brine pH ~ 7.5
- X-29-4: silica precipitated by addition of 2.5×10^{-4} M Fe(III) to unflashed brine at pH = 8.0
- X-29-5: silica precipitated by addition of 2.5×10^{-4} M Al to unflashed brine at pH = 8.0

- b. X-29-1: silica precipitated by addition of NaOH to spent brine, final pH ≥ 9.0

Figure 38. Cumulative removal of Mg from silica scale deposit from the turbine nozzle inlet at HGP-A as a function of HCl concentration.

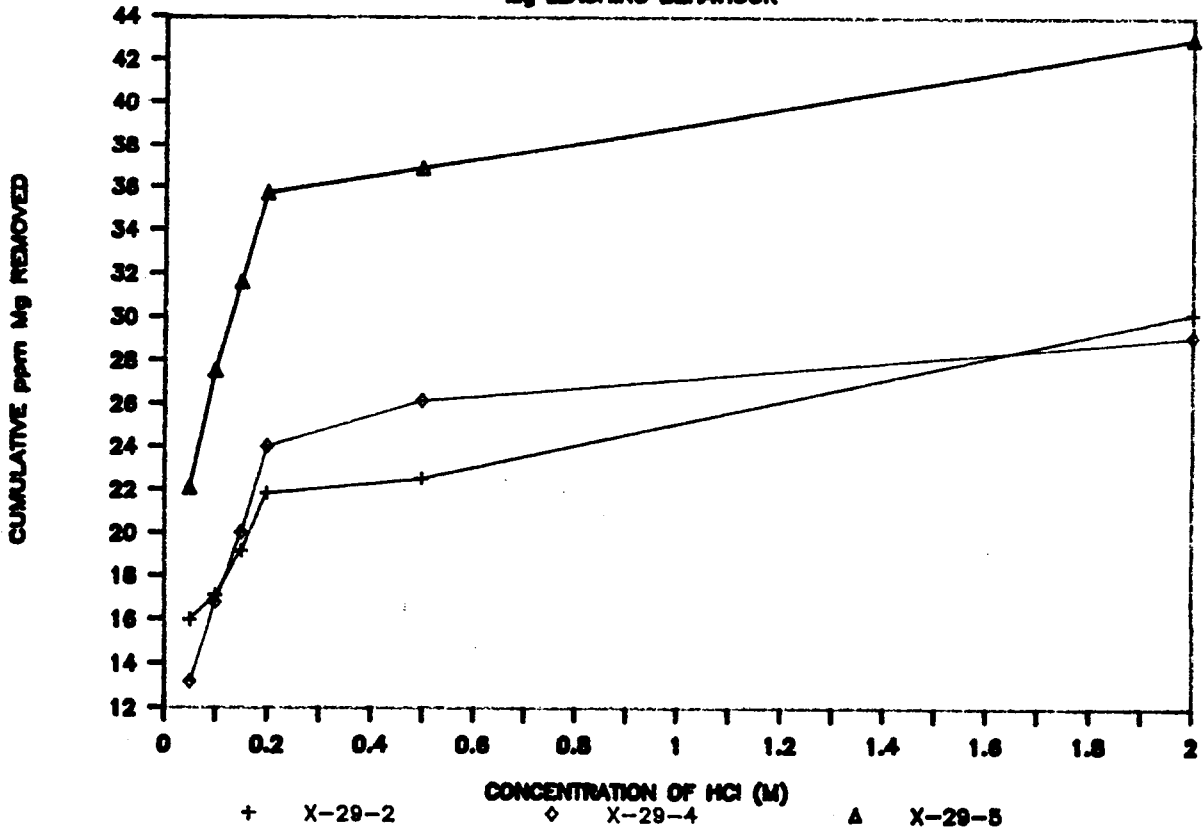
GEOHERMAL SILICA PROJECT

Mg LEACHING BEHAVIOUR



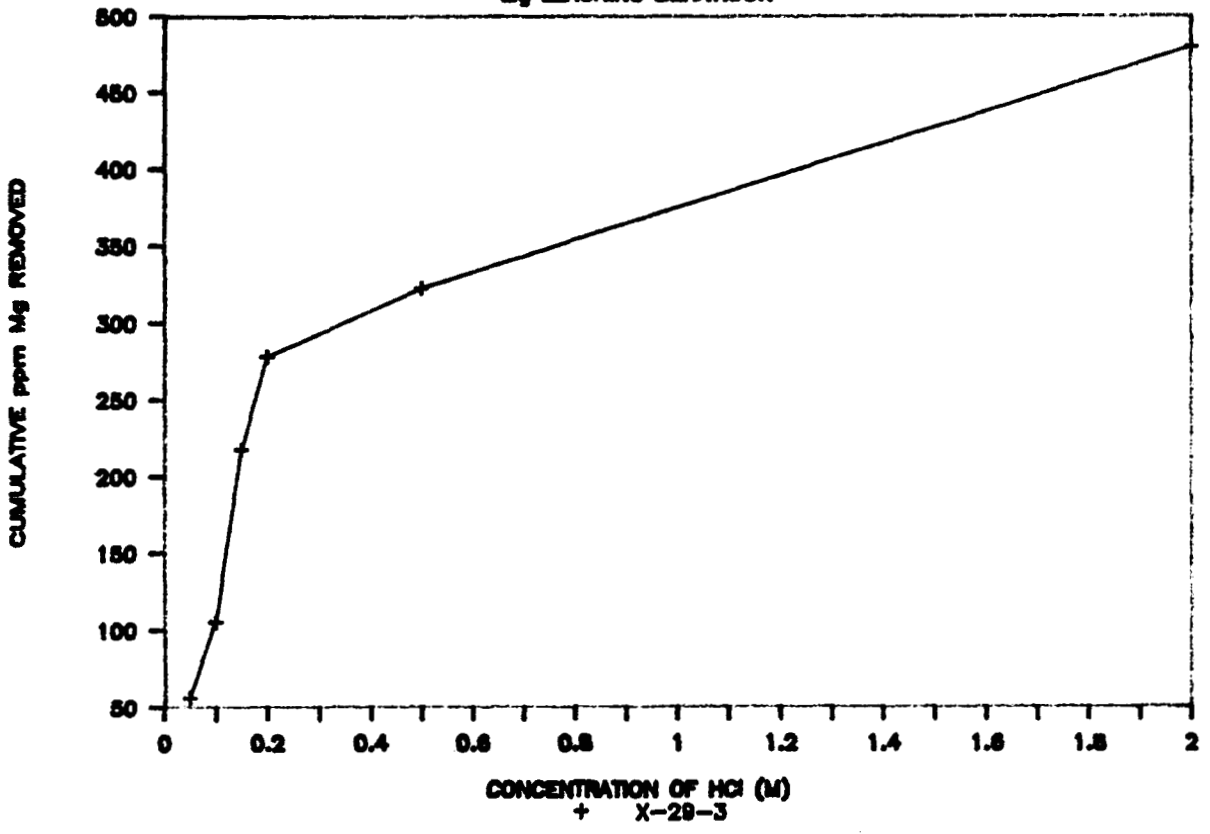
GEOHERMAL SILICA PROJECT

Mg LEACHING BEHAVIOUR



GEOTHERMAL SILICA PROJECT

Mg LEACHING BEHAVIOUR



+ X-29-3

approximately a third of this amount was removed by the leachings. This is in contrast to the nearly complete removal of Mg in the samples discussed above. The difference in behaviour exhibited by sample X-29-1 both in its nearly threefold higher initial Mg content and in the decreased lability of the Mg may result from several factors. 1) The higher pH of formation may lead to a more favorable environment for adsorption and incorporation of the high charge to size ratio of the Mg cation; 2) the use of NaOH to enhance precipitation may affect the Mg content by a contribution of this metal from the NaOH itself; 3) the use of NaOH may alter the ordering of the precipitate in such a way that a greater fraction of the Mg is tightly bound to the silica and thus not readily removed by leaching with HCl. The shape of the removal curve is not significantly different from those for the other enhanced precipitation samples and indicates that the fraction of Mg removed is in similar structural environments as those of the aforementioned samples, and is readily leached from the sample matrix. The presence of tightly bound Mg in the silica is evident when one examines the removal curve for sample X-29-2 which is given in Figure 37b. The initial concentration of 93 ug/g Mg in this sample of a natural scale formed at the air-water interface of the atmospheric flash tank represents mostly Mg which is not readily leached. Again less than a third of the Mg is removed by the experimental procedures. Such a behaviour leads us to believe the contention made above that a fraction of the Mg is incorporated in non-surface sites. Slow formation of the deposit favours a more ordered internal structure for the silica which in turn leads to more tightly bound constituents of the sample.

In a manner similar to the behaviour described above, samples X-29-4 and X-29-5 do not exhibit complete removal of Mg incorporated in the precipitate. The removal curves for these two samples are also shown in Figure 37b and show a leaching pattern similar to all samples formed by enhanced precipitation. In these two samples over half of the Mg is leached out with most of it removed by the 0.5 M HCl step. The amount of labile Mg is in contrast to that of other rapidly formed silica samples (except X-29-1); the reason for this is presently unclear but may be related to the fact that these samples were generated from unflashed brine. The composition of unflashed brine is different from that of spent fluids in which total dissolved solids are more abundant. From this we would expect a greater incorporation of metal ions in the silica from the latter. This very fact though may contribute to the observed pattern as the higher Na (most abundant constituent) concentration in spent brine may displace Mg from the electrical double layer of the silica by mass action and lead to its lower abundance in silica generated from unflashed brine. The lesser removal of Mg from X-29-4 may result from preferential attraction to Fe-rich silica due to its more negative surface charge characteristics.

The sample which appears to contain the most tightly bound Mg is X-29-3. The removal curve for this sample of scale from the turbine nozzle inlet is shown in Figure 38. The gradual leaching of Mg from the silica as a function of HCl concentration is that which would be anticipated from the origin of the sample. The scale deposited over an extended period of time and had the opportunity to incorporate a much larger quantity of Mg than any of the other silica precipitates studied. The initial Mg concentration of 1385 ug/g is extremely high when one considers the depletion of Mg in the geothermal fluids at HGP-A. As previously discussed in the section on Ca, we believe that Mg is preferentially removed from the fluids by the silica deposit as a result of its higher charge to size ratio. This is reflected by the lower concentration of Ca in the turbine nozzle inlet scale as compared to that from the flash tank. Since sample X-29-3 formed slowly, the incorporated Mg is probably held tightly within the structure of the silica and not easily accessible. This is reflected in the data of Figure 38. Although the slope of the leaching curve

is greater in the dilute HCl section of the plot, a significant amount of Mg is removed with the 2.0 M HCl leaching step. This supports a stronger binding environment for the Mg. Although the sample is not crystalline, as evidenced by X-ray diffraction analysis, the ordering of the silica structure is anticipated to be much greater than in any of the other deposits evaluated in this investigation.

CONCLUSIONS AND RECOMMENDATIONS

Silica precipitates have been formed from geothermal fluids at the Hawaii Geothermal Project Well-A (HGP-A) by enhanced flocculation induced through the addition of inorganic species such as hydroxide, and polyvalent metal cations such as Al(III) and Fe(III). The precipitates incorporate a variety of other metal constituents of the brine besides those added to enhance flocculation. The concentration of metals in the silica precipitates is a function of two main parameters: 1) the concentration of the metal available for incorporation (i.e. the concentration in the fluids during precipitation) and 2) the surface charge characteristics of the silica precipitates formed. Naturally deposited scale at HGP-A bears a number of similarities to rapidly precipitated silica but generally contain higher concentrations of other metals as a result of extended scavenging by the silica over long periods of time.

Metal species adsorbed onto the surface or incorporated within the silica structure are held by a variety of forces. Univalent metal cations such as Na and K are primarily present as counter-ions neutralizing the electrical double layer of the silica; divalent cations such as Ca and Mg are held by a mixture of stronger electrostatic and chemisorptive forces which result from the high charge to volume ratio of these species and to the specific affinity of their hydroxy complexes for the silica surface; hydroxy complexes of polyvalent metal cations of Fe and Al can be held by variable strength chemisorptive attractions, or as for certain divalent cations by actual incorporation into the silica crystal structure through bridging mechanisms. When electrostatic attractions to the surface of the silica dominate, a higher charge to volume ratio for any given cation relative to other cations will favor preferential adsorption. Among metal hydroxy complexes chemisorption may lead to preferential adsorption as opposed to simple electrostatic attraction. As a result of the above suggested mechanisms the following sequence of increasing affinity for the silica is proposed: Sodium < Potassium < Calcium < Magnesium < Aluminum < Iron. It must be noted that in the case of the proposed cross-linking of the silica structure by metal ions the sequence changes to Sodium < Potassium < Magnesium < Calcium < Aluminum < Iron.

Further studies on the incorporation and leaching behaviour of other species are gravely needed. Species of interest should include elements of environmental interest such as heavy metal cations which are present at trace levels within the geothermal fluids and which are known to be effectively scavenged and concentrated by silica, as well as polyatomic anionic species such as arsenate, arsenite, selenate, selenite, etc... Leaching experiments aimed at evaluating the behaviour of the silica in other solutions in a manner analogous to the present study should be performed. Suggested media should include simulated ground-waters of varying acidity, other inorganic acids such as nitric acid, and ammoniacal solutions of varying concentrations. It would also be beneficial if specific solvents which might be used by industrial concerns during the purification of the silica prior to processing and/or manufacturing could be identified and their effect on the silica evaluated. Any further studies undertaken should also address kinetics of the processes of adsorption as well as desorption and be designed in such a manner as to exercise tighter control over this often neglected yet important parameter.

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