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Edited by

K. LOUWRIER, E. STAROSTE and J. D. GARNISH
*Directorate-General for Science, Research and Development,
Commission of the European Communities, Brussels, Belgium*

and

V. KARKOULIAS
*Directorate-General for Energy,
Commission of the European Communities, Brussels, Belgium*

A STUDY OF SCALING DUE TO HIGH ENTHALPY GEOTHERMAL FLUIDS

N. ANDRITSOS, A. MOUZA and A.J. KARABELAS
Chemical Process Engineering Research Institute, P.O. Box 19517 and
Chemical Engineering Department, University of Thessaloniki
GR 540 06 Thessaloniki, Greece

Summary

Analyses of samples from the Milos 2MWe Geothermal Plant have been used to characterize the scale forming in various parts of the plant. Heavy metal sulfides are the dominant compounds of scale close to the point of primary fluid flashing, whereas silicates and silica tend to dominate at the other end of the plant (point of fluid reinjection). Laboratory experiments with a typical sulfide (PbS) show a very strong effect of pH and concentration on the rate of scale formation. Similar results are obtained in silica polymerization experiments. Data on the effect of other factors on PbS scale formation and on silica polymerization are summarized. A practical implication of this work is that pH control of geothermal fluids may provide an effective means of combating the scaling problem.

INTRODUCTION

The formation of hard and tenacious scale in pipes and in equipment of geothermal plants constitutes the main obstacle in the economic exploitation of many geothermal fields. The scaling problem is encountered in almost every geothermal installation, but it can be more acute in plants handling high enthalpy brines.

Scale formation can be controlled, at least partially, with careful design of the plant and choice of appropriate operating conditions, with chemical modification of the geothermal fluid, and finally with periodic shut-downs of the plant and removal of the scale with mechanical or chemical means.

The main objective of the work presented here is to document the nature and the composition of the scale encountered in a fairly typical high enthalpy field, such as the Milos geothermal field, and to understand the mechanism of scale formation. Moreover, it is expected that a combination of field measurements and of scale characterization with carefully controlled laboratory experiments (performed with the most abundant scale constituents, i.e. heavy-metal sulfides and amorphous silica), will help evaluate possible ways of scale prevention. In this paper we report on the following aspects of the work carried out so far:

(1) Chemical analyses of geothermal fluids of the Milos Power Plant, chemical and morphological analysis of various scale samples, and evaluation of parameters affecting scale deposition.

(2) Experimental deposition studies of lead sulfide in a pipe at ambient conditions. These experiments provide invaluable information on the mech-

anisms responsible for the PbS deposition and on the factors which influence scaling.

(3) Experiments on silica polymerization kinetics which is of great significance in the formation of silicious deposits.

Related work is also in progress on two-phase flow, which is important in clarifying the mechanism of scaling and in providing valuable information for the design and operation of geothermal plants. Results of this work have been summarized in progress reports to EEC and will not be included here due to space limitations.

SCALE FORMATION - GENERAL CHARACTERISTICS

The geothermal fluid under the reservoir conditions of high pressure and temperature is usually saturated in slightly soluble salts. The main cause of scale formation is the "flashing" of the fluid, that is, both the continuous pressure drop along the pipe due to flow and the sudden pressure reduction of the fluid at a certain point (henceforth referred to as "the main flashing point"), which is dictated by the operating conditions. Flashing results in the simultaneous reduction of the brine mass, in the drop of temperature and finally in the pH increase of the brine, due to the release of CO_2 and H_2S. Consequently, many compounds in the brine become supersaturated and tend to precipitate and to deposit onto the pipe wall.

The scale composition is usually very complex and depends heavily on the brine composition, the pressure and temperature of the system, and the distance from the main flashing point. Low or medium enthalpy fluids (T<150 C) with low salinity usually form a scale rich in carbonates. Silicate minerals are formed from high enthalpy and low salinity fluids, while from high salinity fluids scales rich in heavy metal sulfides and silica are deposited (Owen and Michels, 1984).

The scale can cause a significant increase in the pressure drop due to both reduction of the pipe cross-section and increase of the roughness of the pipe walls. It is noteworthy that the scales have usually a rippled appearance. A direct consequence of the scaling may be the decline of the well productivity and the substantial cost of pipe cleaning and maintenance. High scaling rates are often observed at specific locations, such as the piping immediately downstream of the main flashing point, and the reinjection pumps and their piping manifolds.

A characteristic form of scaling (observed in some parts of the Milos Geothermal Plant) are "assemblages" of broken scale segments of various sizes and thicknesses, apparently transfered from upstream locations and subsequently cemented together by further deposition. These segments result from growth of scale in distinct layers with different physical properties (composition, hardness, specific density). Long term variation of brine properties seems to be responsible for the formation of these layers.

CHARACTERISTICS OF SCALES FROM THE MILOS GEOTHERMAL PLANT

A detailed discussion of scale characteristics from the Milos Geothermal Plant can be found elsewhere (Karabelas and others, 1988). The main observations and conclusions of this work can be summarized as follows:

- The highest scale formation rates appear to be in the two-phase flow line (downstream of the flashing valve), in the hot-water collecting tank (downstream of the high pressure separator), and in the reinjection pumps. (Figure 1).
- Scale deposition in this facility is found to consist mainly of heavy metal sulfides (Pb, Zn, Fe and Cu) and of silicate minerals (basically amorphous silica).

-Heavy metal sulfides dominate in the vicinity of the main flashing point while the percentage of silica tends to increase towards the rein-jection well.

-There are indications of a "crystallization fouling" type of mechanism in the deposition of heavy metal sulfides.

-Primary flashing at ~24 bar results in significant reduction of scale formation, compared with that for primary flashing at ~8 bar at which silica supersaturation is much greater. As expected, the main constitu-ent of scale when flashing at 8 bar is amorphous silica.

Additional analyses and observations of scale samples from the Milos Plant are included in a recent report by Andritsos (1988). Most of the sam-ples analyzed were collected between the hot water collecting tank and the sampling point No 2, as illustrated in Figure 1, covering a pipeline length of ~200 m.

The main crystalline phases, identified by X-ray Diffraction in most of the samples, are heavy metal sulfides (PbS, α-and β-ZnS and $Fe_{0.95}S$). Ad-ditionally, most of the samples show a broad band at about 4 A, indicative of amorphous silica. The chemical analysis of the samples is presented in Table I.

Special attention must be paid to samples No 4 and No 8. The former comes from a vertical pipe section, 18 m downstream of the control valve. It consists of several layers, but with two very distinct bands. The upper band (sample No 4A), having a rippled appearance and a thickness of ~7 mm, is a moderately hard and dark-grey material with obvious crystalline grains. Comparison of its composition with that of other samples has re-vealed that this band was formed during plant operation at 24 bar. Its main crystalline compounds are $Fe_{0.95}S$, β-and α-ZnS and PbS. The ~30 mm thick lower band is a light colored, brittle material, which consists of amorphous SiO_2, crystalline SiO_2, NaCl, KCl and FeS_2. The scale deposit-ed on the turbine blades (sample No 8) consists primarily of $CaSO_4$, FeS_2 and Fe_3O_4. Small quantities of NaCl and CrO_2 were also identified. The presence of Cr and Ni in this sample supports the idea that both these ele-ments as well as the iron are corrosion/erosion products of the turbine ma-terial.

LABORATORY STUDIES OF PbS DEPOSITION

Lead sulfide can comprise a significant part of the scale deposited on metal surfaces in most geothermal plants, provided that lead ions exist in the brine even at low concentration. The objective of this part of the pro-ject is to determine and evaluate the parameters which influence PbS depo-sition, under conditions that partly imitate the sudden supersaturation of the brine at the main flashing point. Initial deposition rates are calculated from the measured mass of PbS deposited on specially designed coupons. The lead sulfide sol is formed by mixing two liquid streams containing sul-fide and lead ions in stoichiometric ratio and in various concentrations. Ad-ditional information on the deposition pattern is obtained by scanning elec-tron micrographs of the deposit-covered surfaces of small interchangeable plugs.

Details on the experimental techniques and the effects of pH and flow velocity can be found in Andritsos and Karabelas (1988a), while the effects of time, of PbS concentration and of the substrate are reported in Andritsos and Karabelas (1988b). Results of typical runs for a certain concentration and various pH values are shown in Figure 2.

Figure 3 illustrates the effect of flow rate on deposition, showing a linear dependence of deposited mass on flow rate. This is indicative of a "diffusion-controlled" type of mechanism. Additional evidence in support of

this mechanism is that the measured maximum deposition rate for a certain concentration is very close to the computed diffusion rate of the elementary PbS crystal unit and comparable to the diffusion rate of the lead ion.

The influence of PbS concentration on deposition is clearly shown in Figure 4b, where initial deposition rates for three PbS concentrations are presented. The maximum deposition rates are obtained in the region of pH values where a dramatic change of the sol absorbance takes place (shown in Figure 4a), indicating a complete dissolution of PbS. It is important to note that the maximum deposition rates appear to be proportional to the concentration. Direct crystallization on the pipe surface seems to be the dominant mechanism of the deposition for pH values lower than that of the maximum deposition rate, while at higher pH particle deposition and particle agglomeration also occur. As is well known, with increasing particle size (due to agglomeration) the deposition rate tends to decrease and this is indeed observed in the experiments. Moreover, some very loosely bound agglomerates are observed to deposit on the pipe surface at pH values higher than that of maximum deposition.

EXPERIMENTS ON SILICA POLYMERIZATION KINETICS

As is well known silica precipitation and scaling depends on the polymerization rate of monomer SiO_2 or H_4SiO_4. Factors affecting the rate of polymerization are the pH, degree of monomer supersaturation, salinity, temperature and foreign particles or seeds (Makrides, Turner and Slaughter, 1980). An experimental set-up was constructed to carry out silica polymerization tests at elevated temperatures and pressures, i.e. at conditions close to those occurring in geothermal plants. The reaction pressure in this set-up can be adjusted in the range 1 to 10 bar by means of high pressure nitrogen gas, while the maximum working temperature is 150 C.

Experiments are performed to study the effect of initial concentration, pH and temperature. Some results are shown in Figure 5. As expected the rate of monomer disappearance is quite strongly dependent upon the initial monomer concentration, which influences the degree of supersaturation. On the other hand, the temperature does not seem to have a strong influence on the net rate of silica polymerization since two opposing effects are taking place. Indeed, a temperature rise tends to enhance the mobility of molecules thus increasing the intrinsic reaction rate, but simultaneously the SiO_2 solubility increases thus reducing the degree of supersaturation.

Preliminary experiments have also been performed to study the effect of seeding the solution with colloidal particles. Figure 5b shows that seeding with colloidal spherical silica particles of diameter ~20 nm (Ludox TM by DuPont) causes a rather drastic reduction of the so-called "induction period" of polymerization, effectively increasing the rate of silica precipitation. This is important from the practical standpoint since geothermal fluids almost always contain suspended solid particles from the reservoir or rapidly forming heavy metal sulfide grains.

There is a strong pH effect on silica polymerization, as is also shown in Figure 5c, which can be explained as follows. The effect of pH on silica solubility is not significant for pH values smaller than 8.5 (e.g. Iler, 1979). However, the pH affects the rate of polymerization reaction which seems to be catalyzed by the OH^- ions. The maximum polymerization rates are observed in the pH range 5 to 8, but a reduction occurs below pH=5 with the minimum reaction rate observed at pH<3 (Makrides, Turner and Slaughter, 1980). It is clear therefore that pH control of geothermal fluids may be used to reduce silica deposition rates.

CONCLUSIONS AND COMMENTS

The main conclusions which are drawn from this work so far are as follows:

(1) The PbS deposition at ambient conditions is strongly dependent on pH and total concentration. The same trend regarding pH and concentration is obtained from the silica polymerization experiments.

(2) For a fixed PbS concentration, appreciable deposition occurs in a limited range of pH values of about two pH units. The maximum deposition rate is observed at the pH value of complete dissolution of PbS.

A practical implication of this work, provided that the same deposition features and trends in the results hold at high temperatures and high salinity fluids, is as follows: To prevent sulfide scale formation it seems necessary to reduce the pH by about one unit below the pH value at which practically all the scale forming heavy metal ions are in solution. This is demonstrated in Table II in which the concentration of heavy metals in the Milos geothermal brine is compared with the solubility of the corresponding sulfides, at pH values 5.3 (the brine pH) and 4.3. The solubilities are calculated according to Helgeson (1969) for a fluid with 2M salinity, at 230°C. The pH reduction is expected to have a beneficial effect on silica deposition as well.

A second implication is that by increasing the pH of the brine, and possibly adding a coagulant, the sulfides will tend to agglomerate thus facilitating their separation by mechanical means. It is very likely that silica will behave similarly in the same pH range (5.5-7.5). Obviously more work is necessary to firm up the above conclusions and to arrive at economically acceptable solutions of the scaling problem.

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Karabelas, A.J., N. Andritsos, A. Mouza, M. Mitrakas, F. Vrouzi, and K. Christanis (1988). Characteristics of scales from the Milos Geothermal Plant. International Workshop on Deposition of Solids in Geothermal Systems, 16-19 August, Reykjavik.

Makrides, A.C., M. Turner, and J. Slaughter (1980). Condensation of silica from supersaturation silica acid solutions. J. Colloid Interf. Science, 73, 345-367.
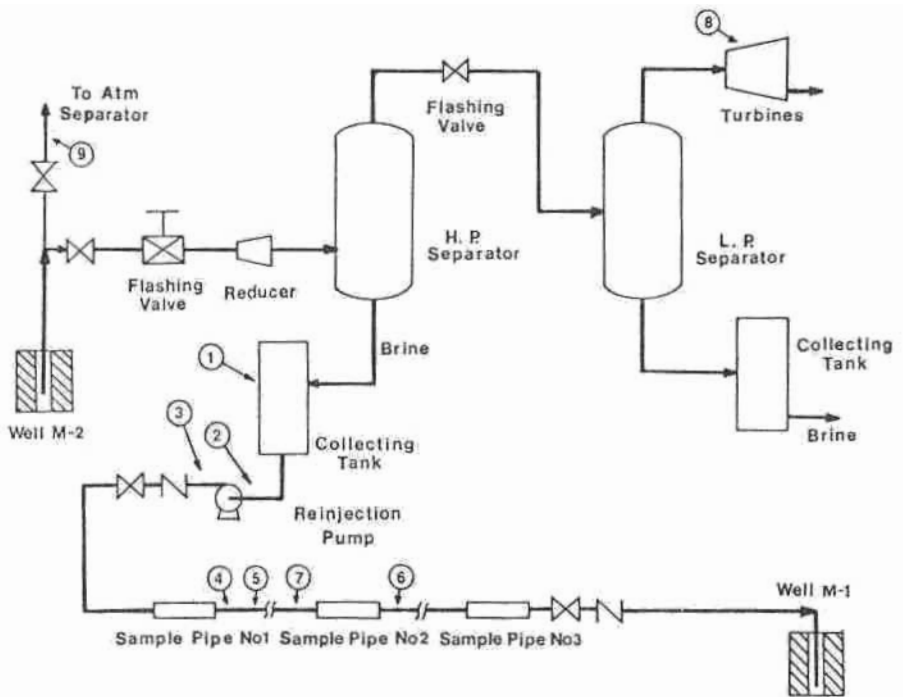
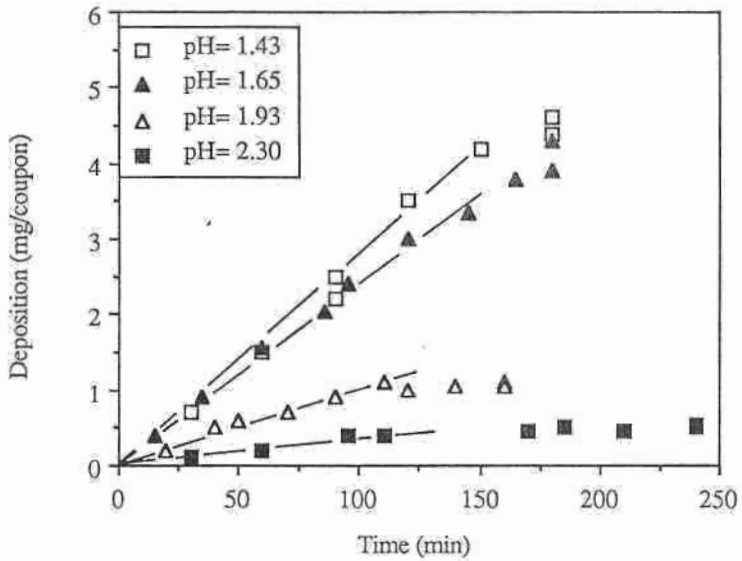Figure 1. Flow diagram of the Milos 2MWe pilot plant showing the sampling points

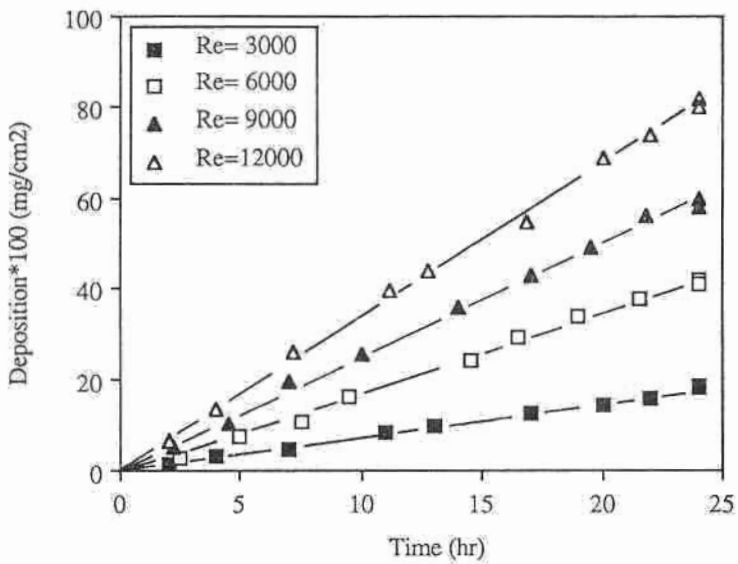Figure 2. Effect of pH on deposition (C= 26.5 ppm, Re= 6000).

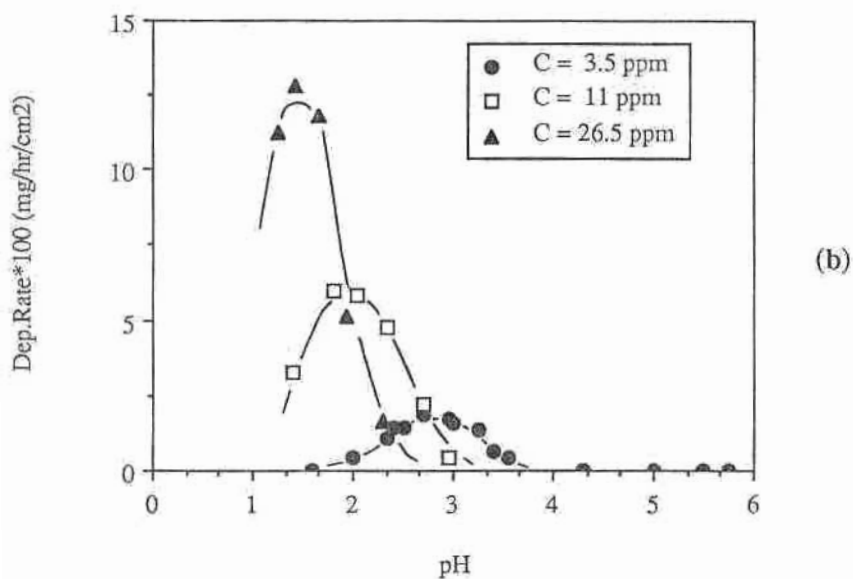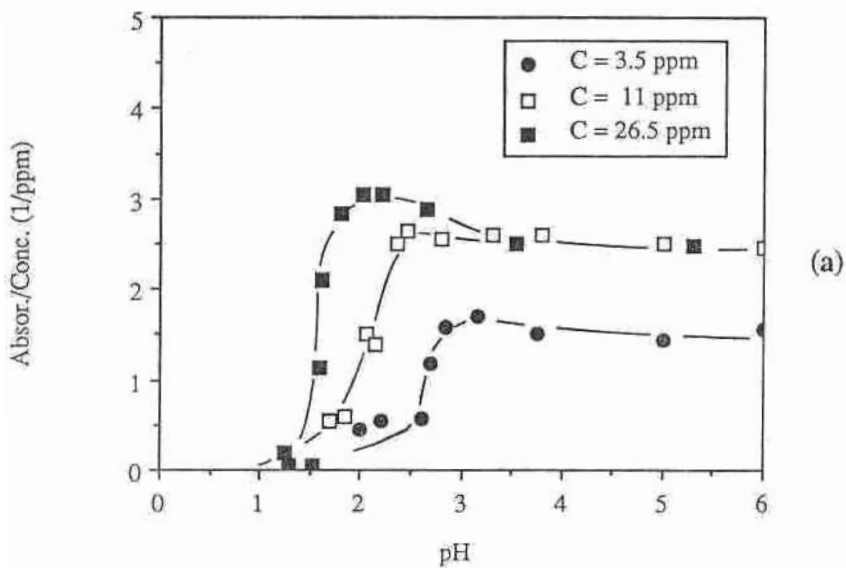Figure 3. Effect of flow rate on deposition (pH=3.0, C=3.5 ppm)

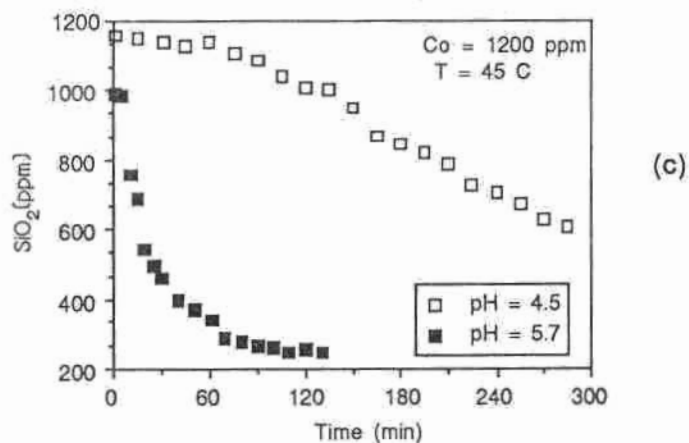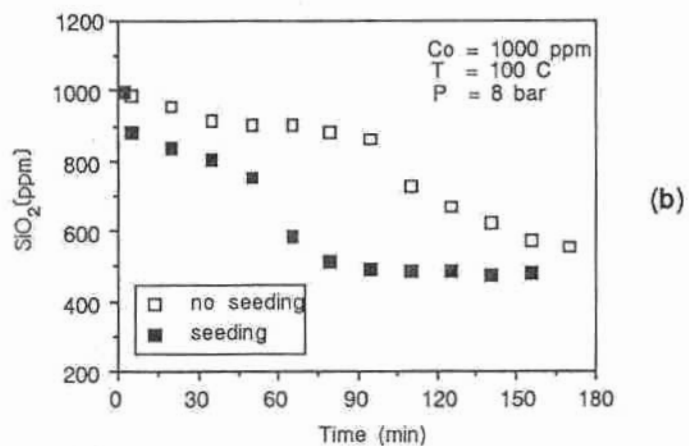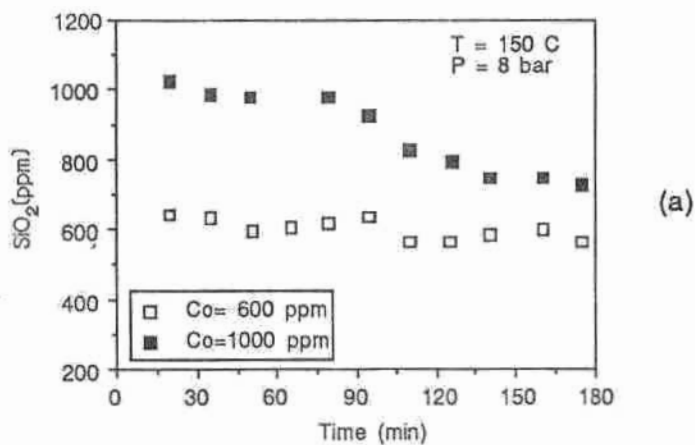Figure 4. Effect of pH on sol absorbance (a) and on deposition rate (b).

Figure 5 . Effect of various factors on Silica polymerization:
(a) initial monomer concentration, (b) seeding, (c) pH.

TABLE I: Chemical Analysis of Scale Samples

Component	Composition (wt %)								
	SAMPLE								
	1	2	3	4A	4B	6	7	8	9
Na	1.0	0.8	1.8	1.1	4.7	2.3	1.7	1.0	0.1
K	0.3	0.3	0.6	0.4	1.2	0.6	0.6	0.3	0.0
Mg	0.0	0.2	0.2	0.2	0.1	0.3	0.4	0.0	0.0
Ca	0.2	0.1	0.2	0.1	0.9	0.1	0.2	7.5	0.0
Mn	0.1	0.6	0.6	0.5	0.3	0.8	1.0	0.1	0.1
Pb	1.2	3.7	1.1	3.0	0.3	3.0	1.5	0.2	7.2
Fe	18.5	30.0	35.8	39.6	6.9	27.1	23.6	29.8	14.8
Zn	4.7	13.5	3.1	7.8	0.1	13.0	7.3	0.2	7.8
Cu	0.2	0.6	0.8	0.3	0.1	0.1	0.3	0.1	0.3
Ni	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Cr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0
Ag	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Si	24.4	6.4	8.6	4.6	32.3	7.2	14.8	5.0	20.3
Cl	1.9	1.2	2.9	2.2	9.2	3.6	2.7	1.4	0.1
$SO_4^=$	0.2	0.3	4.0	1.0	0.4	0.5	0.5	16.9	0.3
TOTAL	52.7	57.7	59.7	60.8	56.5	58.6	53.6	64.3	51.1

TABLE II: Comparison between the solubilities of heavy metal sulfides and the concentration of the corresponding heavy metals in the brine.

Metal	Concentration in brine (ppm)	Solubility, ppm M^{++}	
		pH=4.3	pH=5.3
Pb	1.8	7.3	0.75
Zn	3.3	39.0	4.10
Fe	20.0	17.5	1.80