SIMULATION OF THE GEOCHEMICAL PROCESSES OF THE GEOTHERMAL BRINES WITHIN THE EVAPORATION PONDS AT THE GEOTHERMAL FIELD OF LOS AZUFRES, MEXICO

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ABSTRACT

With a total of more than 95 %, amorphous silica represents the major mineralogical component of the sediments at the bottom of the evaporation ponds at the geothermal field of Los Azufres, Mexico. The metals and non metals Fe, As, Cs, and Mn as further components are encountered in decreasing abundance. Modifications of its primary, white or greyish color towards reddish or brownish tones can be explained by the presence of alguas and the input of terrestrial material. Observed secondary processes of dissolution and redeposition of some mineral aggregates can be explained by changes of the saturation grade of the brine water.

The programm PHREEQC was applied for the simulation of the geochemical behaviour of the geothennal brines within the evaporation ponds of the geothermal field of Los Azufres, Mexico. The cooling of the fluids from an input temperature of 90°C towards an average pond temperature of 40°C as well as fluid losses by evaporation processes into the atmosphere were considered. Differences in the chemical composition of the inflowing and outflowing fluids can be attributed to the loss of approximately 10 % of the water volume during its residence time within the evaporation ponds. Cooling effect represents an insignificant factor for the precipitation or dissolution of the species as part of the fluid - solid system.

The extraction of the metals and non metals from the sediments showed their variations in dissolution behaviour: The elements Tl, Cs, Sr and Rb are very soluble, whereas U, Ag, Cd, Ga and Hg become accumulated in the residual paction of the sediment. Ni, Cr, Bi and Mo get dissolved from carbonate compounds. The major part of the metals and non metals get easily dissolved under neutral pH conditions, which are common in surface environments. Due to the elevated concentrations of Mo, Hg, Tl, and As, special treatment techniques will be required for the final deposition of the sediments in the future.

1.0 INTRODUCTION

The geothermal field of Los Azufres, which is located 220 km NW of Mexico City, has been used for geothermal exploration since 1982. Directly after their rise, the geothermal fluids will be separated at the surface, whereby the vapor phase is used for electricity production and the water phase is stored in evaporation ponds before reinjection. In 1995, 11 wells were used for reinjection, 13 for study purposes and 24 production wells generated an installed total capacity of 98 MW.

The evaporation ponds form part of the production cycle at the geothermal field of Los Azufres: After its separation fiom the vapor phase, the geothermal water is temporary deposited within the ponds for its final reinjection into the reservoir. As a consequence, the fluids are cooled down fiom an initial input temperature of >90°C to an output temperature of approximately 40°C. The target of this preliminary deposition is mainly the cooling of the fluids. As a secondary effect of the evaporation and cooling processes, the accumulation of sediments can be observed at the bottom of the ponds.

In this study, it was investigated whether

- the pond sediments represent precipitation products of the geothermal brines and/or represent transported clastic, terrestrial sediments from the surroundings of the ponds.
- precipitation processes cause the enrichment of metals and no metals within the sediments.
- evaporation processes and / or temperature changes are the principal reasons for the depletion or enrichment of metals and no metals in the pond sediments.
- dissolution processes within the sediments by fluid phases could cause a mobilization of the fixed trace elements.
- the existence of a potential environmental risk for the final deposition of the residual sediments.

2.0 METHODS

The computer program PHREEQC was applied to simulate following geochemical processes:

- The precipitation potential and the saturation index of the mineral species of the geothermal brines.
- Comparison of the chemical composition of the pond sediments with the simulated PHREEQC results.
- The effect of evaporation and changes in temperature on the chemical composition of the geothermal brines.

The geochemical simulation required following pre-studies:

- Geochemical analysis with ICP-MS of the inflowing and outflowing geothermal brines of the evaporation ponds.
- Raster electrone microscope (REM) and diffractometer analysis to determine the microscopical and mineralogical composition of the sediments.
- Extraction procedure (method after Salomons and Forstner, 1980) to determine:
  a) the major and minor elemental composition of the sediments
  b) the solubility behaviour of the metals and non-metals of the sediments under different environmental conditions.

3.0 RESULTS

3.1 Microscopical and Mineralogical Analysis

A microscopical, mineralogical and geochemical characterization of the sediments was realized as part of this study. The sediments of the ponds Az-2, Az-5, Az-22, Az-25 and Az-28 are characterized by fibrous, elongated aggregates with an average length between 20 µm and > 50 pm. These structures are typically formed by the primary crystallization of precipitated mineral aggregates from the brines. Secondary processes cause the formation of knobby, rounded structures, which cover and transform the single needles to a homogeneous, amorphous mass. Crater shaped structures at the mineral surfaces are interpreted as the consequence of secondary dissolution and redeposition processes of some mineral aggregates, which are probably caused by changes of the saturation grade of the brine water.

Modifications of its primary, white or greyish color towards reddish or brownish tones can be explained by the presence of alguas and the input of terrestrial material. The occurrence of small concentrations of clay minerals, such as smectite, can be interpreted as minor terrestrial input.

3.2 Chemical Composition of the Sediments and their Solubility Behaviour

The metal and non-metal composition of the pond sediments, which was determined by its dissolution with concentrated HNO_3 and HCl, is shown in Table 1 (Birkle, 1998). Amorphous silica represents the major chemical component with a total of more than 95 %. The metals and non-metals Fe, As, Cs, and Mn as further components are encountered in decreasing abundance. Their concentrations are elevated in comparison to natural sediments. Especially the abundance of Mo, Hg, Tl, and As will require special treatment techniques for the final deposition of the sediments in the future.

Table 1. Average metal and no metal concentrations of the pond sediments of the units Az-2, Az-5, Az-22, Az-26, and Az-28.

Element	Average concentration (mg/kg)	Element	Average concentration (mg/kg)	Element	Average concentration (mg/kg)
As	72.8	Se	0.36	Cs	10.6
Cu	4.2	Hg	0.28	W	4.3
Zn	3.3	Co	0.23	Tl	0.26
Mo	3.0	Cd	0.10	Bi	0.01
Pb	2.7	Mn	7.1	Th	0.08
Ba	1.5	Ga	0.20	U	0.02
Ag	1.6	Ge	0.19	Fe	1583
Cr	0.99	Rb	5.5	Si	990000
Ni	0.80	Sr	1.8		

A five-step dissolution sequence with several extraction steps allows the detection of natural chemical combinations and the dissolution behaviour of the precipitated metals and no metals within the sediments. *An* analytical procedure with several extraction steps was carried out according to the method from Salomons and Forstner (1980).

As a result, following solubility and mobility behaviour of the metals and no metals was observed:

- Tl, Cs, Sr and Rb are very soluble.
- U, Ag, Cd, Ga and Hg become accumulated in the residual fraction of the sediment.
- Ni, Cr, Bi and Mo get dissolved fiom carbonate compounds.
- Se, Zn and Cu fiom little reduced phases.
- W, As, Mn, Ba, Pb, Co, Fe, Ge and Th from phases with intermediate reduction.

The most important fact is the high solubility behaviour of the trace elements: The major part of the metals and non-metals get easily dissolved under neutral pH conditions, which are common in surface environments.

3.3 Simulation of the Geochemical Processes with PHREEQC

Dissolved mineral species of the geothermalfluids

Results from the chemical analysis and physical-chemical parameters such as temperature, pH and the redox potential of the geothermal brines of the pond system Az-22 were applied as input factors. The database WATEQ4F (Ball and Nordstrom, 1991), including data for the aquatic species, gas and mineral phases and also their saturation indices were used for the calculation of the species composition of the geothermal brines. The results of the geochemical simulation comprises a physical-chemical description of the aquatic phase, the thermodynamic equilibrium constants, activities of the species, and the saturation indices of the mineral phases.

The main species characteristics of the simulated Az-22 system are as follows (Birkle, 1998):

- The elements Ca, Cl, Cs, K, Li, Mg, Na, Sr and Rb are distributed with more than 96% as free cations and anions within the brines.
- Elements with high oxidation steps, such as As (+V) and Se (+IV) are encountered as $HAsO_4^{2-}$, $H_2AsO_4^-$, $HSeO_3^-$ and SeO_3^{2-}.
- Ba and Si are distributed to more than 97% as elemental $H_3BO_3^0$, $H_4SiO_4^0$.

Manganese shows a large variety of species in the geothermal brines (Figure 1). The main part is formed by Mn^{2+}**(81%)**. **High** Cl$^-$ and HCO$_3^-$ concentrations explain the abundance of MnCl$^+$ **(13.5%)** and MnCO$_3^+$ **(2.5%)**.

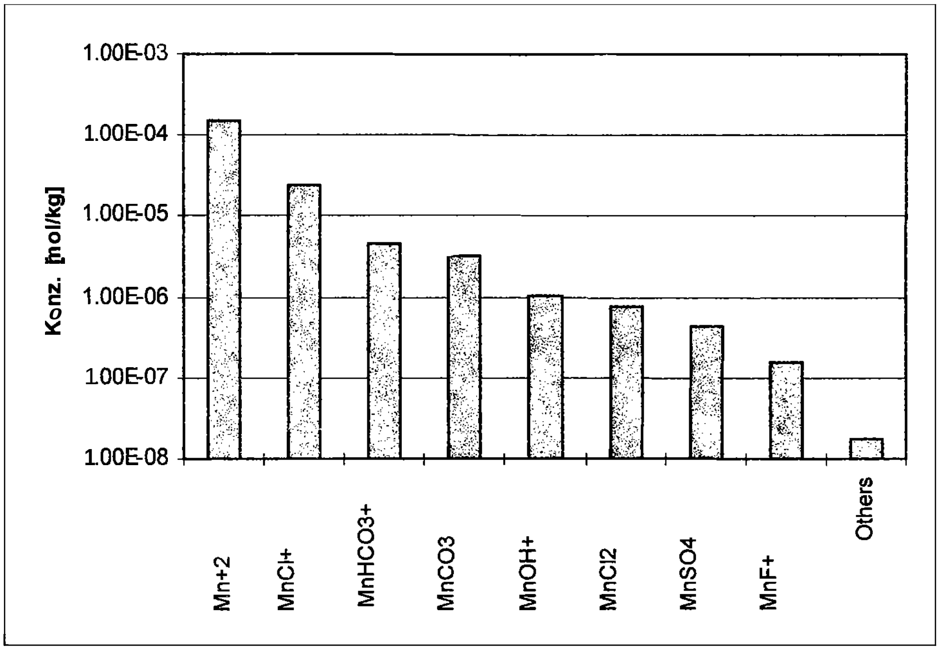

Figure 1. Concentration of the Mn (+II) species of the geothermal brine in the pond **Az-22.**

Saturated mineral phases

A potential precipitation behaviour was registered for several mineral modifications of silice: Chalcedony, cristobalite, quartz, silicagel and amorphous SiO$_2$ are characterized by saturation index values between **- 0.15** and **+ 0.53** (Table 2). Oher potential minerals to precipitate in the evaporation ponds are several iron-oxides and iron-hydroxides (Fe$_2$O$_3$, FeOOH), MnCO$_3$ and selenium.

Table 2. Saturation index (SI), product of ion activity (IAP) and solubility constant (KT) *of* the over saturated mineral phases in the geothermal brines *of* the pond Az 2.

Mineral	SI	log IAP	log KT	Chem. Formel
Chalcedon	0.53	-2.48	-3.01	SiO_2
Cristobalit	0.47	-2.48	-2.96	SiO_2
$Fe(OH)_{2.7}Cl_{0.3}$	3.91	12.78	8.87	$Fe(OH)_{2.7}Cl_{0.3}$
Goethit	4.32	15.23	10.91	FeOOH
Hämatit	14.17	30.47	16.30	Fe_2O_3
Magadiit	3.06	-11.24	-14.3	$NaSi_7O_{13}(OH)_3{:}H_2O$
Maghemit	0.26	30.47	30.22	Fe_2O_3
Magnetit	15.35	37.16	21.86	Fe_3O_4
Ni_2SiO_4	0.13	10.86	10.73	Ni_2SiO_4
Quarz	0.81	-2.48	-3.30	SiO_2
Rhodochrosit	0.92	-10.37	-11.29	$MnCO_3$
Rhodochrosit (d)	0.02	-10.37	-10.39	$MnCO_3$
Se (s)	4.39	-55.44	-59.84	Se
Silicagel	0.03	-2.48	-2.51	Si02
SiO_2 (a)	-0.15	-2.48	-2.33	SiO_2

This simulation results indicate following:

- The microscopical and mineralogical composition of the sediments is confirmed by the simulation of the geochemical behaviour of the geothermal brines and the existence of potential, over-saturated minerals.
- The reason for the precipitation processes must be the temporary or permanent oversaturation of the brine water.

Effects of evaporation and temperature

The microscopical, mineralogical and chemical studies from above confirm the origin of the pond sediments as a typical precipitation result of the geothermal brines. Possible reasons for changes in the saturation behaviour of the geothermal brine are a) the decrease in temperature of the brine water from > 90°C (pond inflow) to 40°C at the pond outflow and/or b) evaporation and volume reduction of the brine water. The chemical composition of the inflowing and outflowing brine water at the pond unit Az-28 were used respectively as input and output value for the geochemical simulation with PHREEQC (Parkhurst, 1995) (Table 3).

Table 3. Comparison of the simulation PHREEQC results with the real measured concentrations of the pond system Az-28 (in mg/l). The simulation **was** carried-out extracting 10% of the total brine volume. The last column gives he percental deviation of the PHRREQC results from the real output v ues.

Element	**Geothermal brine Input b 2 8**	**Geothermal brine Output Az-28**		**Percental deviation of the PHREEQC simulation**
Cl	2778	3100	3107	+ **0.2**
Na	1631	1767	1677	- 5.1
K	457	487	511	+ 4.9
Ca	2.4	2.5	2.68	+ 7.2
Li	22.6	23.5	25.2	+ 7.2
F	14.0	10.0	15.64	+ 56.4
SO_4	24.0	25.0	8.67	- 65.3
Si	151	144	78.9	- 45.2
B	265	272	295.8	+ 8.8
As	22.0	24.0	24.56	+ 2.3
Fe	0.024	0.035	0.027	- 22.9
Ag	0.0005	0.0006	0.00055	- 8.3
Ba	0.0382	0.0730	0.043	- 41.1
Cd	0.0021	0.0033	0.0023	- 30.3
cs	2.66	2.82	2.97	+ 5.3
cu	0.014	0.039	0.016	- 58.9
Mn	0.015	0.016	0.016	0.0
Ni	0.0117	0.0108	0.013	+ 20.4
Pb	0.0042	0.0081	0.0047	- 41.9
Rb	3.76	3.97	4.19	+ 5.5
Se	0.282	0.324	0.315	- 2.8
Sr	0.218	0.231	0.243	+ 5.2
Zn	0.146	0.142	0.163	+ 14.8

The evaporation process was simulated extracting a fixed percentage of distilled water from the geothermal brine in several simulation steps. The temperature decrease **from** 90 to 40°C was simulated in two steps. Various simulations were carried out to get an accordance between the real outflow concentrations and the PHREEQC output values. The last column of Table 3 shows the deviation of the simulated results from the real measured concentrations of the geothermal brine.

The results are as follows (Birkle, **1998):**

- Decreases in temperature cause little changes in the chemical composition of the geothermal brine.
- Evaporation represents the principal factor for changes of the saturation behaviour of the brine and such for the accumulation of precipitates at the bottom of the ponds.
- The loss of approximately 10% of the total brine volume gives the best accordance between real and simulated values. It explains best the observed chemical variation between the inflowing and outflowing geothermal brines. In general, the deviations are small for major elements, whereas the occurrence of trace elements such as F and SO_4 must be also related to other processes than evaporation.

4.0 CONCLUSIONS

Evaporation processes cause the precipitation **of** different mineral species at the bottom of the evaporation pond at the geothermal field of Los Azufres. The simulation of the geochemical data with PHREEQC confirms the dominance of amorphous silica as precipitated result of over-saturated geothermal brines, but it exists also a precipitation potential for several other mineral species, such as iron-oxides and hydroxides, manganese carbonate and selenium.

Although the sediments consists to more than **90%** of amorphous silica, elevated concentrations of some metals and no metal, such as Mo, Hg, Tl, and As, require remediation procedure for the final deposition of the pond sediments in the future. Extraction experiments indicate the high solubility of several metals and no metals within the sediments, especially TI, Cs, Sr and Rb.

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