Mineralogical–chemical composition and environmental risk potential of pond sediments at the geothermal field of Los Azufres, Mexico

P. Birkle · B. Merkel

Abstract Since 1982, estimated amounts of 9,400 t, 15,000 kg, 720 kg and 105 kg of Si, Fe, As and Cs respectively have accumulated at the bottom of 18 evaporation ponds as part of the geothermal production cycle at Los Azufres. This accumulation is caused by precipitation of brine solutes during the evaporation of 10% of the total pond water volume before its re-injection into the reservoir. Extraction experiments with pond precipitates and geochemical simulations with the PHREEQC program indicate the high solubility of most precipitates under natural environmental conditions. The comparisons with the primary brine composition indicate that less than 1% of most dissolved brine solutes, except for Co, Cu, Mn, Pb, Ag, Fe and Si, are accumulated at the pond bottom. Arsenic has maximum values of 160 mg/kg in the pond sediments, and Mo, Hg and Tl also exceed international environmental standards for contaminated soils. Elevated concentrations and the mobility potential of several metals and non-metals require the application of remediation techniques for the final disposal of the sediments in the future.

Keywords Los Azufres · Geothermal field · Pond sediments · Environmental impact

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Introduction

The geothermal field of Los Azufres, located 220 km northwest of Mexico City, has been used for geothermal exploration since 1982 (Fig. 1). In 1995, 11 wells were used for re-injection, 13 for study purposes and 24 production wells generated an installed total capacity of 98 MW. Directly after their rise to the surface, the two-phase geothermal fluids become separated. The vapour phase is used for electricity production, whereas the water phase is temporarily stored in evaporation ponds before its final re-injection into the deep reservoir. The target of the preliminary deposition of the geothermal brines is mainly the cooling of the fluids from an initial input temperature of >90 °C to an average pond temperature of approximately 40 °C to avoid later scaling problems in the casing of the re-injection wells. As a secondary effect of the cooling process, sediment accumulation can be observed at the bottom of the ponds. As an example, Fig. 2 shows the production cycle of well Az-26 with the production well, separator and silencer units on the left side, the evaporation pond (centre) and the discharging pipeline towards the re-injection well (foreground).
This paper attempts to resolve the following:

- Whether the pond sediments represent precipitation products of the geothermal brines and/or represent transported clastic, terrigenous sediments from the surroundings of the ponds.
- Whether precipitation processes cause the enrichment of metals and non-metals within the sediments.
- Whether evaporation processes and/or temperature changes are the principal reasons for the depletion or enrichment of metals and non-metals in the pond sediments.
- The possibility of re-mobilisation of trace elements, bound in the pond sediments, by secondary dissolution processes.
- The potential environmental risk for the final deposition of residual sediments.

Methods

Six sediment samples were taken from the bottom of five evaporation ponds at the geothermal field. Eighteen ponds

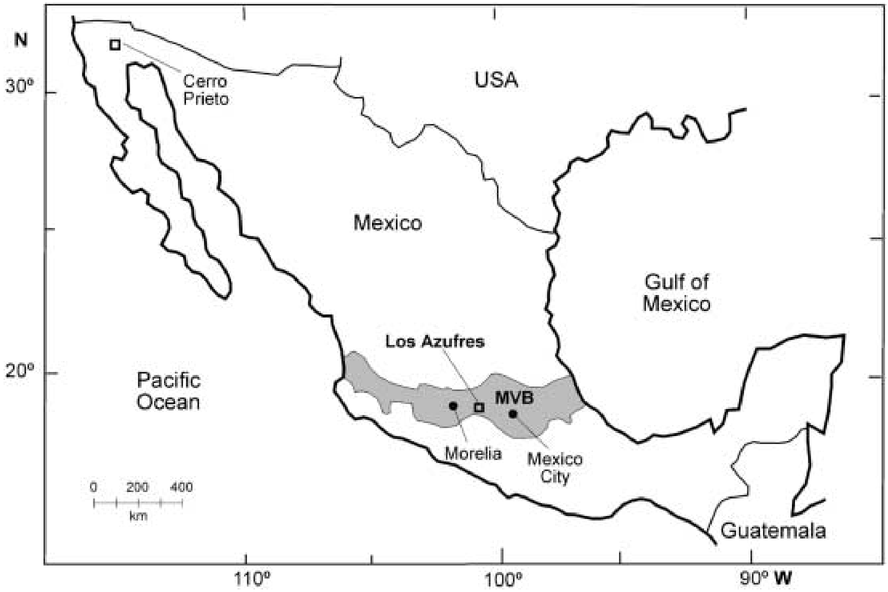

Fig. 1
Location of the Los Azufres geothermal field in the central part of Mexico and western part of the Mexican Volcanic Belt (*grey*)

of the geothermal field are used in turn and are recharged by a brine mixture of varying production wells. The location of sampled ponds and related production wells is shown in Fig. 3. The samples are named according to the adjacent production well. Table 1 shows the contributing production wells for the evaporation ponds (wells indicated by italics contribute intermittently), the sample locality, the water depth of the sample site, and the colour of the sediment.

The microscopic and mineralogical composition of the sediments was determined by raster electron microscope (REM) and diffractometer analysis at the Institute of Geology and the Institute of Mineralogy respectively, both at the Technical University of Freiberg in Germany. A five-step extraction procedure (method after Salomons and Förstner 1980) was applied to determine the metal and non-metal composition of the sediments and to characterise the solubility behaviour of the metals and non-metals under different environmental conditions. The extracts were analysed with the ICP-MS method at the Institute for General Ecology in Tharandt/Saxony, Germany.

Fig. 2
Geothermal production cycle, including the deep well Az-26, the fluid separator, and the emitted vapour phase in the background. The evaporation pond and the discharging pipeline, conducting the brines by gravity towards the re-injection well, are shown in the foreground

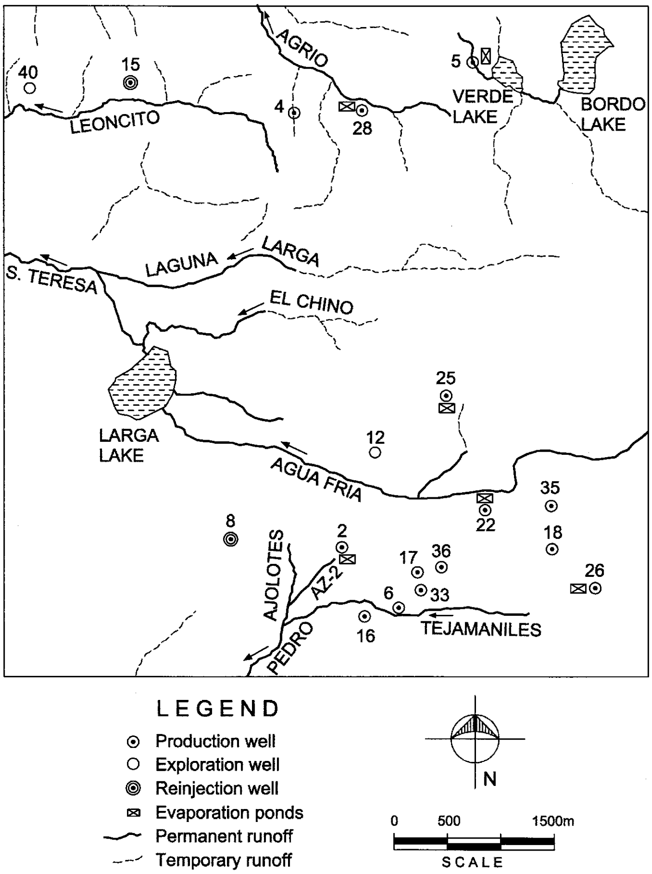

Fig. 3
Location of the sampled evaporation ponds, and the adjacent production and re-injection wells, as well as permanent and temporary runoff systems of the geothermal field

Table 1
Details of the sampled sediments

Sediment samples	Contributing wells	Sample locality	Water depth (cm)	Sediment colour
Az-2	Az-2, *Az-33, Az-37, Az-38, Az-46*	Inflowing section	10	White
Az-5	Az-5, *Az-48*	Inflowing section	5	White – dark brown
Az-22 (1)	Az-22, *Az-35, Az-55*	Edge of pond 1	30–40	Beige
Az-22 (2)	Az-22, *Az-35, Az-55*	Outflowing section of pond 2	10	Reddish
Az-26	Az-26, *Az-31*	Edge of the pond	10–20	Light–dark brown
Az-28	Az-28, *Az-4*	Inflowing section	10–20	White – brown

Geochemical processes were simulated with the computer program PHREEQC (1) to determine the precipitation potential and saturation index of the mineral species of the geothermal brines, (2) to evaluate the effect of evaporation and changes in temperature on the chemical composition and the precipitation behaviour of the brines, and (3) to compare the analysed chemical composition of the pond sediments with the simulated PHREEQC results. As a requirement for the geochemical simulations, hydrochemical analyses of the inflowing and discharging geothermal brines at the evaporation ponds were carried out using the ICP-MS method.

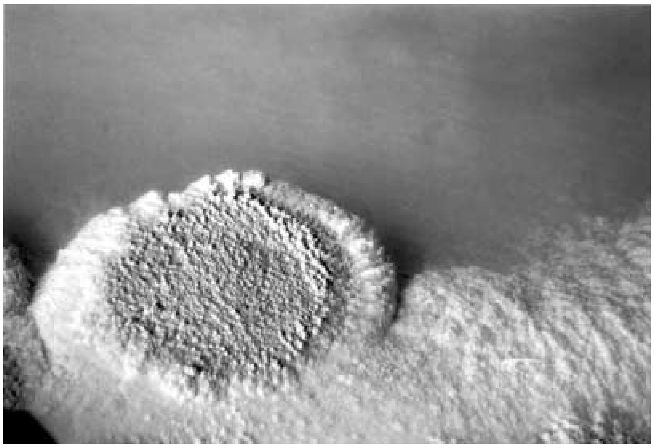

Fig. 4
Cauliflower-shaped mineral aggregate at the border of the evaporation pond of the well Az-2. Diameter of the silica formation: ca. 1.0 m

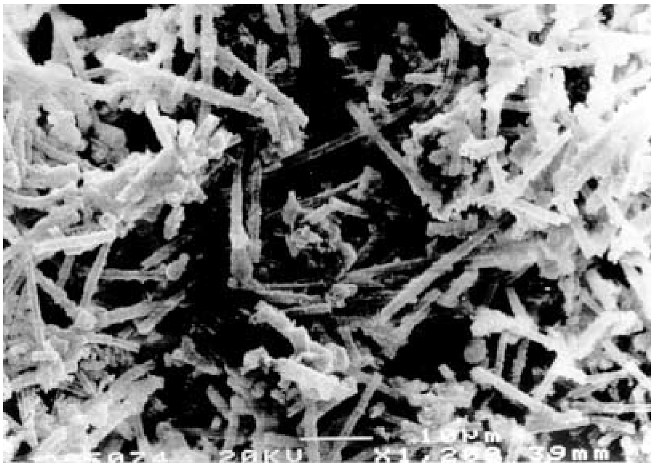

Fig. 5
REM illustration (×1,200) of amorphous silica needles, formed by primary crystallisation processes

Structural and mineralogical features

On a macroscopic scale, the sediments can be distinguished by their colour and their morphological shape. The colours vary from white to reddish to dark brown (Table 1). Modifications of the primary, white or greyish colour towards reddish or brownish tones can be explained by the presence of algae and the input of terrestrial material. The greenish to yellowish colour of the Az-2 pond sediments, zoned parallel to the pond border, is related to the growth of algae and/or bacteria. The bottom of the lagoon is covered by white to light greyish, stromatolite or cauliflower-shaped, rounded sediment structures (Fig. 4). In contrast, the Az-22 pond appears like a tropical coral reef, formed by elongated, irregular needles or fibres of centimetre and decimetre size.
Microscopically different types of primary and secondary structures can be distinguished:

- Primary needles and stalks: Sediments of the ponds Az-2, Az-5, Az-22, Az-25 and Az-28 are characterised by fibrous, elongated aggregates with an average length between 20 and >50 μm. Most of the fibrous structures seem to be hollow in their interior. Figure 5 shows a detailed REM image (×1,200) of the needle structures of the Az-22 sediments. These are probably formed by the primary crystallisation of mineral aggregates, precipitated from the brines.
- Primary layers and crusts: Besides stalk structures, the growth of crusts or horizontal layers at the ponds Az-2, Az-5 and Az-28 is related to primary precipitation and/or secondary growth processes. Isolated small plates (<3 μm) of the Az-5 sediments are welded together to a compact layer as part of an advanced growth process.
- Secondary tubers and layers: Secondary processes cause the formation of knobbly, rounded structures, which cover and transform single needles to a homogeneous, amorphous mass.
- Secondary dissolution: Crater-shaped structures at the mineral surfaces are interpreted as the consequence of secondary dissolution and re-deposition processes of

mineral aggregates, which are probably caused by changes of the saturation grade of brine water. Figure 6 (sediment Az-5, ×1,200) shows a ball like aggregate (diameter: 160 μm) with multiple, crater-shaped excavations on its surface. The growth of small crystals within the crater structures indicates the fast, temporary alternation between dissolution and re-deposition processes. The temporary undersaturation of the geothermal fluids causes the dissolution of existing crystals, whereas an increase in the ion concentration can cause the continuing precipitation of oversaturated minerals.

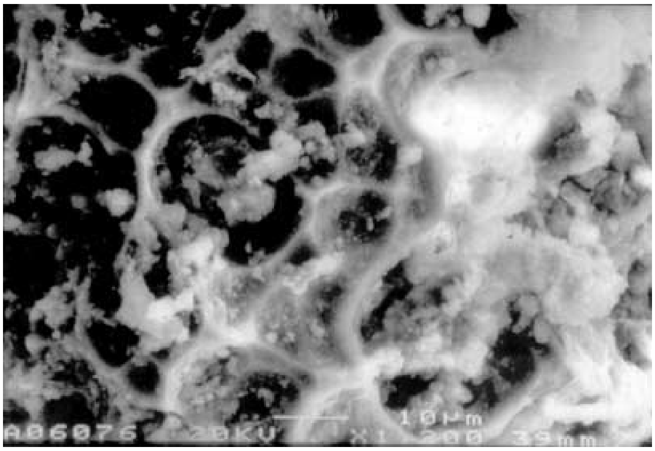

Fig. 6
REM illustration (×1,200) of ball-like, silica aggregate (diameter 160 μm). The small craters on its surface are consequences of secondary dissolution processes under undersaturated conditions, whereas the small crystal plates inside the craters form part of a subsequent crystallisation event

Chemical composition and quantification of the sediments

Semi-quantitative diffractometer analysis confirmed a chemical composition of the pond sediments with more than 95% of amorphous silica. Minor peaks of halite, representing concentrations between 1 and 2% of the sample, were encountered for the Az-2, Az-22, Az-26 and Az-28 sediments. The elevated clay content of the Az-5 sample is confirmed by the dark brown sediment colour and by the distinct smectite peak (at 14°) with an estimated percentage of 10 to 15% for the entire sample. The occurrence of small concentrations of clay minerals, such as smectite, can be interpreted as minor terrestrial input from the surroundings of the evaporation pond.

Metals and non-metals were extracted from the pond sediments with concentrated HNO_3 and HCl, and were analysed with the ICP-MS technique (Birkle 1998). Table 2 shows the average metal and non-metal concentrations of the sediment samples Az-2, Az-5, Az-22, Az-26 and Az-28. Amorphous silica is the major chemical component, and Fe, As, Cs and Mn represent minor components (in decreasing order). Their concentrations are elevated in comparison to natural sediments.

Based on field observations and measurements, the following parameters were used to calculate the total mass of metals and non-metals accumulated within 18 evaporation ponds of the geothermal field of Los Azufres:

- Number of evaporation ponds: 18
- Average pond size: 600 m^2
- Total pond area: 10,800 m^2
- Average sediment height: 1 m

Table 2
Trace element concentrations of the geothermal brines and sediments, as well as the sediment fraction

Element	Brine		Sediments		Sediment fraction (% of total brine)
	Average (mg/l)	Total (1985–2000) (kg)	Average (mg/kg)	Total (1985–2000) (kg)	
Cr	11.8	1,116	1.0	9.65	0.86
Mn	26.1	2,469	7.1	70.7	2.86
Co	1	95	0.2	2.3	2.43
Ni	14	1,325	0.8	8.04	0.61
Cu	16.1	1,523	4.2	41.8	2.74
Zn	49.9	4,721	3.3	32.7	0.69
Ga	2.8	265	0.2	2.04	0.77
Ge	35	3,311	0.2	1.88	0.06
As	19,007	1,798,214	72.8	721.8	0.04
Se	351	33,207	0.4	3.59	0.01
Rb	3,568	337,561	5.5	54.1	0.02
Sr	1,327	125,545	1.8	17.1	0.01
Mo	514	48,629	3.0	30	0.06
Ag	1.1	104	1.6	15.5	14.9
Cd	1.4	132	0.1	0.96	0.72
Cs	3,244	306,908	10.6	105.6	0.03
Ba	57.9	5,478	1.5	15	0.27
W	100.8	9,536	4.3	42.3	0.44
Hg	4.1	388	0.3	2.79	0.72
Tl	30.3	2,867	0.3	2.57	0.09
Pb	4.6	435	2.7	26.3	6.04
Fe	81.3	7,692	1,583.0	15,251	198.3
Si	171,000	16,177,968	999,000	9,431,840	58.3

- Total sediment volume: 10,800 m^3
- Dry density: 2.6 g/cm^3
- Wet density: 1.8 g/cm^3
- Water content: 49%
- Wet weight: 19,440 t
- Dry weight: 9,915 t

Measuring the dry weight of silica (2.6 g/cm^3) and the water content of the sediments (49%), an average wet density of 1.8 g/cm^3 for the sediments was determined. Thus, the total sediment volume of 10,800 m^3 of the 18 ponds corresponds to a wet weight of 19,400 t, with 9,915 t representing the dry weight of the sediments. The total amount of each individual metal and non-metal was derived by using the total sediment weight and the analysed concentration (mg/kg) (Table 2). In comparison to the estimated amount of 9,430 t of amorphous silica, other elements are of minor importance. However, the accumulated amount of some toxic elements, such as arsenic (721 kg) and caesium (105 kg), should be considered for the final deposition of the pond sediments.

Simulation of the geochemical processes

The computer simulation program PHREEQC was applied to determine (1) the origin of the precipitated metals and non-metals as dissolved species of the geothermal brine, (2) minerals with a positive saturation index as potential candidates to become precipitated, and (3) factors, such as changes in temperature or evaporation processes, which cause the accumulation of precipitates at the pond bottom.

Dissolved mineral species of the geothermal fluids

Results from the chemical analysis and physical-chemical parameters such as temperature, pH and the redox potential of the geothermal brines of the Az-22 pond system were applied as input data for PHREEQC (Parkhurst 1995). The database WATEQ4F (Ball and Nordstrom 1991), including data for the aquatic species, gas and mineral phases and their saturation index, was used for the calculation of the species composition of the geothermal brine. The results of the geochemical simulation comprise a physical-chemical description of the aquatic phase, the thermodynamic equilibrium constants, activities of the species and the saturation indexes 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-}.
- More than 97% of B and Si are distributed as elemental $H_3BO_3^0$ and $H_4SiO_4^0$ respectively.
- Manganese shows a large variety of dissolved species in the geothermal brines (Fig. 7). At 81%, Mn^{2+} forms the main portion. High Cl^- and HCO_3^- concentrations of the brines explain the abundance of $MnCl^+$ (13.5%), $MnHCO_3^+$ (2.5%) and $MnCO_3$ (1.8%).

Saturated mineral phases of the geothermal fluids

A precipitation potential was registered for several mineral modifications of silica. Chalcedony, cristobalite, quartz, silica-gel and amorphous SiO_2 are characterised by saturation index values between –0.15 and + 0.53 (Table 3). Other potential minerals to become precipitated in the evaporation ponds are various iron oxide and iron hydroxide modifications (Fe_2O_3, FeOOH), $MnCO_3$ and selenium.

Effects of evaporation and temperature

Microscopical, mineralogical and chemical studies confirm that the pond sediments originate as precipitation products of the geothermal brines. Possible reasons for changes in the saturation behaviour of the geothermal brine are: (1) a decrease of the brine water temperature from >90 °C (pond inflow) to 40 °C at the pond outflow, and/or (2) evaporation into the atmosphere and a subsequent volume reduction of the brine water. The chemical compositions of the inflowing and outflowing brine water at the pond unit Az-28 were used as input and output values respectively for the simulation with PHREEQC (Table 4).
The evaporation process was simulated extracting a fixed percentage of de-ionised 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 the best fit between the real measured concentrations (Table 4: column 3) and the PHREEQC output values (Table 4: column 4). The final column of Table 4 shows the deviation (in %) of the simulated results from the real measured concentrations of the geothermal brine. The deviations are negligible for major elements (Na, Cl, K, Ca) and for most trace ele-

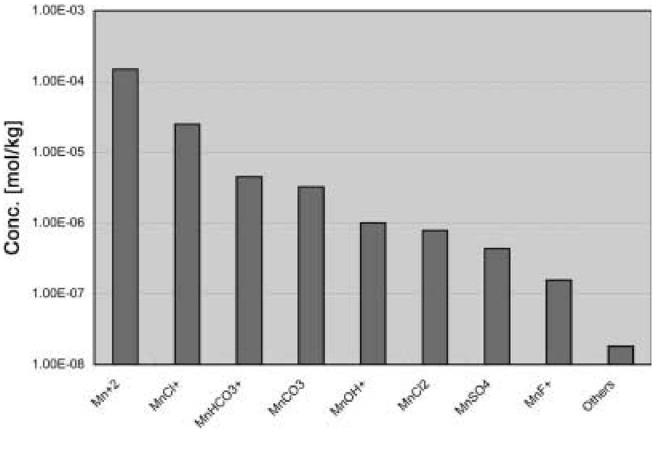

Fig. 7
Concentrations of the Mn (+II) species of the geothermal brine in the Az-22 pond

Table 3
Saturation index (*SI*), product of ion activity (*IAP*), solubility constant (*KT*) and chemical composition of saturated mineral phases in the geothermal brines of pond Az-22

Mineral	SI	Log IAP	Log KT	Chemical composition
Chalcedony	0.53	−2.48	−3.01	SiO_2
Cristobalite	0.47	−2.48	−2.96	SiO_2
$Fe(OH)_{2.7}Cl_{0.3}$	3.91	12.78	8.87	$Fe(OH)_{2.7}Cl_{0.3}$
Goethite	4.32	15.23	10.91	FeOOH
Hematite	14.17	30.47	16.30	Fe_2O_3
Magadiite	3.06	−11.24	−14.3	$NaSi_7O_{13}(OH)_3{\cdot}H_2O$
Maghemite	0.26	30.47	30.22	Fe_2O_3
Magnetite	15.35	37.16	21.86	Fe_3O_4
Ni_2SiO_4	0.13	10.86	10.73	Ni_2SiO_4
Quartz	0.81	−2.48	−3.30	SiO_2
Rhodochrosite	0.92	−10.37	−11.29	$MnCO_3$
Se (s)	4.39	−55.44	−59.84	Se
Silica-gel	0.03	−2.48	−2.51	SiO_2
$SiO_{2\ (a)}$	−0.15	−2.48	−2.33	SiO_2

ments, such as B, As, Ag, Cs, Mn, Rb, Se and Sr. Larger deviations for some elements, such as F, SO_4 and Si, must be attributed to additional physical-chemical processes. The main results are as follows:

- Decreases in temperature cause little change in the chemical composition of the geothermal brine.
- Evaporation represents the principal factor for changes of the saturation behaviour of the brine and the accumulation of precipitates at the bottom of the ponds.
- The simulated decrease of approximately 10% of the total brine volume reflects the best fit between real and simulated values. It explains best the observed chemical variation between the inflowing and outflowing geothermal brines.

Risk potential of the sediments

Mobility and solubility behaviour

The performance of a five-step leaching sequence with several extraction steps allows the detection of natural chemical compounds in soils and sediments and a characterisation of the potential solubility behaviour of metals and non-metals. The analytical procedure was carried out using the methods of Salomons and Förstner (1980). The individual extraction steps reflect the solubility of each chemical compound with different chemical agents:

- Step 1: pH=7.0 with de-ionised water as extraction agent. Soluble by de-ionised water and cationic exchange.

Table 4
Comparison of simulation results with measured concentrations of the pond system Az-28

Element	Geothermal brine		PHREEQC simulation Output conc. (mg/l)	Deviation: simulated vs. measured concentration (% of measured conc.)
	Input conc. (pond Az-28) (mg/l)	Output conc. (pond Az-28) (mg/l)		
Cl	2,778	3,100	3,107	+0.2
Na	1,631	1,767	1,677	−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

- Step 2: pH=7.0 with ammonium acetate as extraction agent. Soluble as carbonic compounds.
- Step 3: pH=5.0 with sodium acetate and acetic acid as extraction agents. Soluble as slightly reduced phases.
- Step 4: pH=2.0 with hydroxyl ammonium chloride as extraction agent. Soluble as moderate reduced phases.
- Step 5: pH=3.0 with ammonium oxalate as extraction agent. Concentrated in the residual phase.

In general, very mobile compounds become dissolved during the initial three extraction steps, whereas immobile components remain in the residual fraction.

Sediment samples from evaporation ponds Az-2, Az-5, Az-22 (two samples), Az-26 and Az-28 were used for the extraction procedure. The concentration of 25 dissolved trace elements was measured after each extraction step with the ICP-MS technique. Figure 8 shows the percentage of the dissolved fraction of Sr, Rb, Cr, Se, Zn, As, Ge and Cd in each of the five extraction steps. Major fractions of Rb and Sr can be dissolved under neutral pH conditions, Cr as carbonic compound, Se under slightly reducing conditions, and As with de-ionised water and moderate reducing conditions. Major portions of Ge (samples Az-22-a, Az22-b, Az-5) become dissolved as moderate reducing phases, whereas most of Ge (samples Az-28, Az-26, Az-2) remains in the residual fraction. The Zn fractions are distributed homogeneously within the extraction steps, whereas most of the Cd content remains within the sediments.

According to their solubility behaviour, the analysed metals and non-metals can be divided into five groups:

- Tl, Cs, Sr, Rb, As, Zn: soluble by de-ionised water + cationic exchange.
- Ni, Cr, Bi, Mo, Zn: dissolved as carbonic compounds.
- Se, Cu, Zn: low reducing conditions.
- W, As, Mn, Ba, Pb, Co, Fe, Ge, Th, Zn: moderate reducing conditions.
- U, Ag, Cd, Ga, Hg: accumulated as sediment residual.

The most important fact is the observed high solubility behaviour of the trace elements. Major portions of the metals and non-metals become dissolved under neutral pH conditions, which are common in surface environments. Another indicator for the precipitation and solubility potential of trace elements is given by the comparison between (1) the total amount of precipitated elements, accumulated during the last 15 years of geothermal production (1985–2000) at the bottom of the ponds (see section above), and (2) the amount of dissolved brine elements that entered into the evaporation ponds during the same time period. The average brine concentrations from the well units Az-2, Az-5, Az-22 and Az-28 and the total amount of dissolved brine elements is shown in Table 2 (columns 2 and 3; Birkle and Merkel 2000). The latter one was derived by assuming a discharge rate of 200 l/s and a total brine volume of 94.6 million cubic metres for the time period from 1985 to 2000. The brine fraction, which precipitates at the bottom of the ponds, is shown in the last column of Table 2. Almost all trace elements (Se, Sr, Rb, Cs, As, Ge, Mo, Tl, Ba, W, Ni, Zn, Hg, Cd, Ga, Cr) remain dissolved in the liquid phase with less than 1% of the brine solutes precipitating. The high solubility behaviour of Tl, Cs, Sr, Rb, As, Zn, as shown in the extraction experiment, reflects the low precipitation potential of those elements. Oxidising conditions of evaporation ponds, caused by strong flow movements of inflowing brines, prevent the oversaturation of Se, Cu, Zn, W, As, Mn, Ba, Pb, Co, Fe, Ge and Th. As shown during the leaching experiment, the elements listed are soluble under reducing conditions. On the other hand, Co, Cu, Mn, Pb, Ag, Si and Fe are accumulated at the bottom of the ponds (2 to 168%, in increasing order). About 58% of the total circulating silica precipitates, which explains the dominance of amorphous silica in the pond sediments. A factor of 198% for Fe indicates the influence of additional Fe sources, such as soil input from the pond edges and bacterial activity.

Comparison with international norms for contaminated soils

Chemical precipitation processes of the evaporating and cooling geothermal brine cause the accumulation of silica and multiple trace elements at the pond bottom. In the near future, the continuous filling up of the evaporation pond could lead to the need for the excavation of the sediment and its final disposal. Several countries, especially the Netherlands (Netherlands Ministry of Housing, Physical, Planing and Environment 1991), Canada (Canada Council of Ministers of the Environment 1991), and Germany (Eikmann and Kloke 1991) have developed national environmental standards to define the maximum permitted limits for the final disposal of contaminated soils (Table 5). The “background value” is defined as the natural occurring concentration, and concentrations in excess of the “threshold value” require ongoing investigations. The “intervention value” indicates the maximal concentration value; to exceed it requires safety or treatment measures (Ewers and others 1993). As a result of the treatment measures, the final “target value” should be obtained.

The Canadian norm is related to agricultural areas, whereas the German BW I and BW II norms illustrate a wide range of values due to their application for different habitats. The spectrum of natural concentrations occurring worldwide was extracted from Scheffer and Schachtschabel (1992), and the background value for selenium from Wilber (1980).

The concentrations of Cu, Zn, Pb, Ba, Ni, Co and Cd of the Los Azufres sediments come within the background composition of natural soils. The elements Cr, Se and Ag partly exceed the natural background values, but the concentrations are still below the “intervention” or “target level”. In contrast, As, with maximum values of 160 mg/kg, in comparison with normal “background concentrations” of 1–20 mg/kg or permissible “threshold values” of

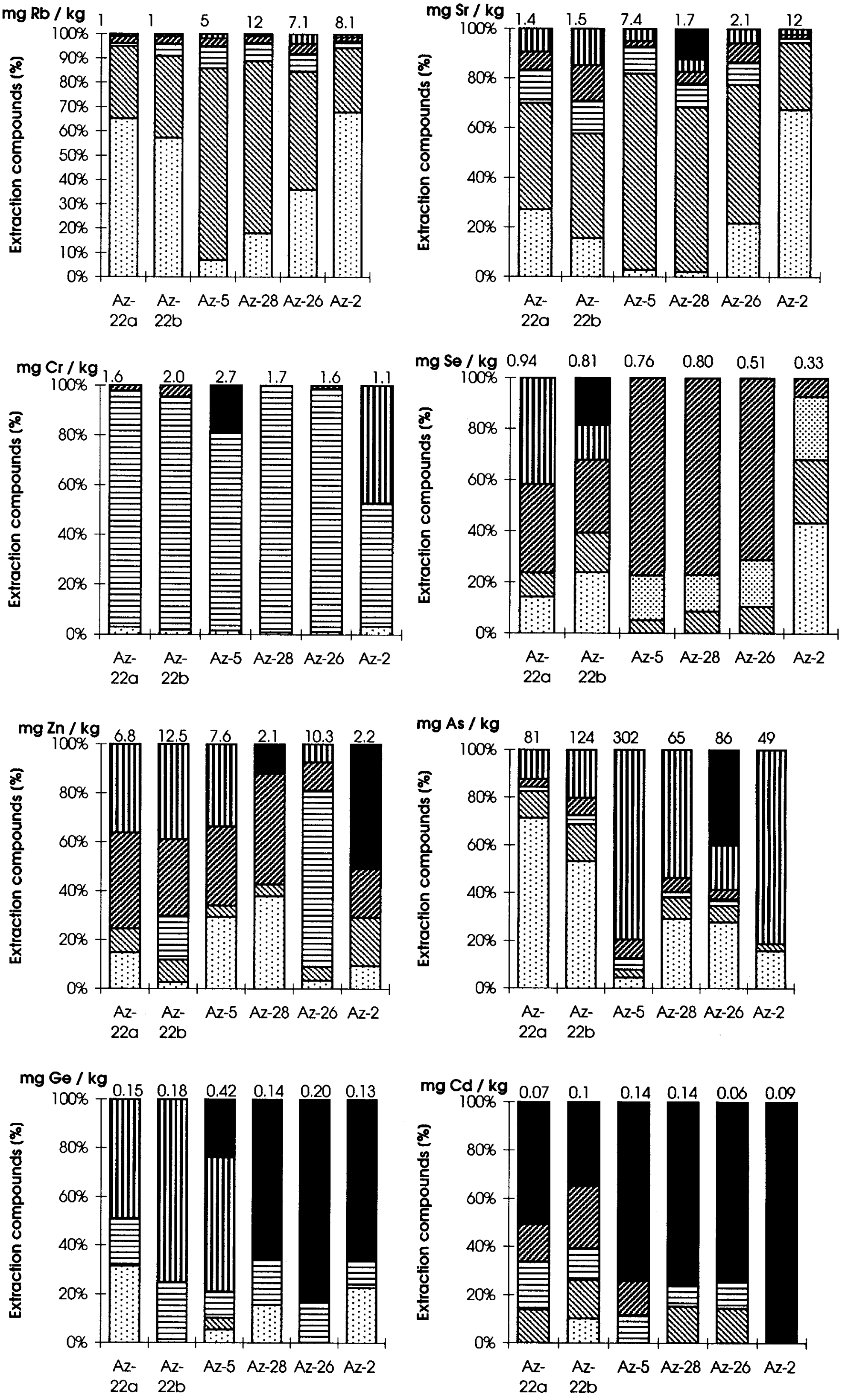

Fig. 8

Results of the five-step extraction procedure for six sediment samples from five different evaporation ponds. The dissolved and residual fraction of each trace element (Rb, Sr, Cr, Se, Zn, As, Ge, Cd) is given in % of the total concentration of the specific element. Step 1 (de-ionised water) – *dots*; step 1 (cationic exchange) – *diagonal from upper left to lower right*); step 2 – *horizontal lines*; step 3 – *diagonal from lower left to upper right*; step 4 – *vertical lines*; step 5 – *filled*

30 mg/kg (Netherlands List), will require intervention measures as well as remediation techniques to comply with international soil standards. Maximum concentrations of 11 and 0.7 mg/kg for Mo and Hg respectively are above the natural "background values", and Mo exceeds slightly the "target values" of the Netherlands List and the Canadian NCSRP (National Contaminated Sites Remediation Program) norm.

Table 5
Comparison of metal and non-metal concentrations of the Los Azufres sediments with international soil standards

	As	Cu	Zn	Mo	Pb	Ba	Ag	Cr	Ni	Se	Hg	Co	Cd
Pond sediments from Los Azufres													
Average concentration (mg/kg)	73	4.2	3.3	3.0	2.7	1.5	1.6	1.0	0.8	0.4	0.3	0.2	0.1
Maximal concentration (mg/kg)	160	10	7.4	11	4.9	6.4	4.2	2.7	1.6	0.8	0.7	0.9	0.1
Background value													
Netherlands List: Reference value A	20	50	200	10	50	200	–	100	50	–	0.5	20	1
Soil value BW I (Germany)	–	50	150	–	100	–	–	50	40	–	0.5	–	1
NCSRP (Canada)	5	30	60	2	25	200	2	2.5	20	1	0.1	10	0.5
Non-contaminated soils (Scheffer and Schachtschabel 1992)	1–15	2–40	10–80	0.2–5	2–60	–	–	5–100	5–50	0.2	0.02–0.5	1–40	0.1–0.5
Threshold value (examination value)													
Netherlands List: Threshold value B	30	100	500	40	150	400	–	250	100	–	2	50	5
Soil value BW II (Germany)	–	50–500	300–2,000	–	200–1,000	–	–	50–400	40–250	–	0.5–10	–	2–10
Intervention value													
Netherlands List: Intervention value C	50	500	3,000	200	600	2,000	–	800	500	–	10	300	20
Soil value BW II (Germany)	–	200–2,000	600–3,000	–	600–2,000	–	–	250–800	200–500	–	10–50	–	5–20
Target value													
Netherlands List	29	36	140	10	85	200	–	100	35	–	0.3	10	0.8
NCSRP (Canada)	20	150	600	5	375	750	20	8	150	2	0.8	40	3

Discussion

In comparison with Cerro Prieto in Baja California State (Fig. 1), which is the largest geothermal field in Mexico and second largest in the world, the amount of accumulated sediments in Los Azufres is very low. In Cerro Prieto, 50% of the total geothermal brine (ca. 700 l/s) is deposited exclusively for evaporation purposes into one large evaporation lagoon (area 14 km^2) (Hiriart and Gutiérrez 1992). In contrast, about 220 l/s circulate through the 18 ponds of Los Azufres with a total surface of ca. 10,800 m^2 (Birkle 1998). The high precipitation rate in Cerro Prieto makes the filling of the lagoon likely in the near future, whereas a steady flow circulation and the variable saturation conditions in the Los Azufres ponds and high solubilities for most elements could maintain equilibrium between precipitation and dissolution processes.

On the other hand, the dominance of amorphous silica as the principal component of the pond sediments camouflages the potential environmental risk for the final deposition of the precipitates. Besides the total accumulated masses of 9,400 t, 720 kg and 105 kg for Si, As and Cs respectively, the elevated concentrations of Mo, Hg, Tl and As, as well as the high mobility of those elements, will require special treatment techniques for the final deposition of the sediments.

The simulation of the geochemical behaviour of geothermal brines and the existence of potentially saturated minerals by PHREEQC confirmed the microscopic and mineralogical composition of the sediments. The reason for precipitation processes within the evaporation ponds must be the temporary or permanent oversaturation of brine water.

Conclusions

Evaporation processes cause the precipitation of a variety of mineral species at the bottom of the evaporation pond at the Los Azufres geothermal field. The geochemical simulation by PHREEQC confirms the dominance of amorphous silica as the major precipitate from saturated geothermal brines, but a minor precipitation potential for other mineral species, such as iron oxides and hydroxides, manganese carbonate and selenium, also exists.

Although the residues consist of more than 90% of amorphous silica, the norm-exceeding concentrations of some toxic metals and non-metals, such as Mo, Hg, Tl and As, require remediation to make final disposal possible in the future.

In comparison to the total amount of circulating geothermal brine, precipitation processes at the bottom of the evaporation ponds are of minor importance. Leaching experiments reflect the high solubility and re-mobilisation potential for most metals and non-metals, especially Tl, Cs, Sr and Rb, whereas U, Ag, Cd, Ga and Hg tend to remain immobile in the residual fraction.

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References

Ball JW, Nordstrom DK (1991) WATEQ4F – User's manual with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural waters. US Geol Surv Open-File Rep 90–129

Birkle P (1998) Herkunft und Umweltauswirkungen der Geothermalwässer von Los Azufres, Mexiko. Wissenschaftliche Mitteilungen, Technical University of Freiberg/Saxony, Germany, Institute of Geology, 6

Birkle P, Merkel B (2000) Environmental impact by spill of geothermal fluids at the geothermal field of Los Azufres, Michoacán, Mexico. Water Air Soil Pollut 124:371–410

Canada Council of Ministers of the Environment (1991) Interim Canadian environmental quality criteria for contaminated sites. Report CCME EPC-CS34, Winnipeg, Manitoba

Eikmann T, Kloke A (1991) Nutzungs- und schutzbezogene Orientierungswerte für Schadstoffe in Böden. In: Rosenkranz D, Einsele G, Haress HM (eds) Bodenschutz-Loseblattsammlung. Erich Schmidt, Berlin

Ewers U, Viereck L, Herget J (1993) Bestandsaufnahme des vorliegenden Richtwertes zur Beurteilung von Bodenverunreinigungen und synoptische Darstellung der diesen Werten zugrundliegenden Ableitungskriterien und -modelle. Institute for Hygiene of the Ruhrgebiet, Gelsenkirchen. Report ordered from the Administration of the Senate for City Planning and Environment

Hiriart G, Gutiérrez PH (1992) An update of Cerro Prieto geothermal field – twenty years of commercial power. Geotherm Resour Counc Bull 5:289–294

Netherlands Ministry of Housing, Physical Planning and Environment (1991) Environmental quality standards for soil and water. Leidschendam, Netherlands

Parkhurst DL (1995) User's guide to PHREEQC – a computer program for speciation, reaction-path, advective transport, and inverse geochemical calculations. US Geol Surv Water Resour Inv 95-4227

Salomons W, Förstner U (1980) Trace metal analysis on polluted sediments. Part II: Evaluation of environmental impact. Environ Technol Lett 1:506–517

Scheffer F, Schachtschabel P (1992) Lehrbuch der Bodenkunde. Enke Verlag, Stuttgart

Wilber CG (1980) Toxicology of selenium: a review. Clin Toxicol 17(2):171–230