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THEORETICAL STUDIES OF CERRO PRIETO BRINES CHEMICAL EQUILIBRIA

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ABSTRACT

We use a chemical equilibrium model, implemented in a compact FORTRAN package called HITEQ, to investigate possible mineral deposition related to prereinjection treatment of Cerro Prieto brines for silica removal. Large saturation ratios of the treated brines with respect to several minerals are indicated by these computations. As a remedy, we propose an inexpensive CO₂ removal scheme aimed at inhibiting carbonate mineral precipitation. This scheme is quantitatively discussed with the aid of HITEQ. We conclude that the proposed treatment is both technically and economically feasible.

INTRODUCTION

Surface equipment scaling and formation damage due to mineral deposition are risks normally associated with the reinjection of geothermal brines (Howard et al., 1979; Cuellar, 1976). Prereinjection treatment of the brines can provide a solution to these problems (Quong et al., 1978; Weres et al., 1980) which are essentially site-specific due to the wide variation in chemical composition found in geothermal reservoirs (Ellis and Mahon, 1977; Wahl, 1977). Because of our involvement in the Mexican-American Cooperative Project we are interested in prereinjection treatment of Cerro Prieto brines. A scheme for silica removal from separated brines, based on an increase of the natural pH, is presented elsewhere in these Proceedings (Weres and Tsao, 1980). In this paper we study the potential for scaling induced by the silica removal treatment and find it significant. We then propose and discuss a way, which we find both technically and economically feasible, to avoid this potential problem.

The chemical equilibrium model we used in this study is described in the next section. The important mineral saturation ratios and the proposed treatment are discussed in the last section.

THE CHEMICAL MODEL

The adopted model will be described in detail elsewhere (Iglesias and Weres, in preparation). The basic assumption is that of thermodynamic equilibrium. Depending on the values of the thermodynamic variables, the system may consist of a compressed liquid solution, a liquid in equilibrium with a gas phase, or a gas. In a typical two-phase situation the liquid phase contains dissolved nonvolatile components as well as noncondensable gases, and the gas phase is a mixture of steam and volatile gases. Dissociation and complexing take place in the liquid according

to the reactions of Table 1. The gases dissolved in the liquid phase equilibrate according to Henry's Law with the vapor phase (Table 2); steam is assumed to be present at the vapor pressure corresponding to the actual temperature. The total pressure is estimated as the sum of the partial pressures of the gaseous components. The total enthalpy is estimated as the sum of the water (liquid and/or steam) enthalpy and of the enthalpies of the gaseous components. The heats of dissolution are neglected. The activities of the dissolved species are linked to the corresponding concentrations via activity coefficients computed on the modified Debye-Huckel approximation. Conservation of mass and of charge provide the remaining necessary equations.

This model has been implemented in a compact, fast FORTRAN package called HITEQ. The data base covers the range 0 to 300°C. Input parameters are confining pressure, total enthalpy, composition, and (optional) pH. The output provides temperature, enthalpies of water, steam and noncondensable gases, partial pressure of the gas phase components, steam and water masses, pH, ionic strength, liquid concentrations of the dissolved species, and saturation ratios of calcite (CaCO₃), aragonite (CaCO₃), witherite

TABLE 1. SOLUTION REACTIONS*

	log K(100°C)
NH ₃ + H ₂ O = NH ₄ ⁺ + OH ⁻	-4.868
H ₂ S = HS ⁻ + H ⁺	-6.624
H ₄ SiO ₄ = H ₃ SiO ₄ ⁻ + H ⁺	-9.097
H ₃ BO ₃ = H ₂ BO ₃ ⁻ + H ⁺	-8.950
H ₂ O = OH ⁻ + H ⁺	-12.257
CO ₂ + H ₂ O = HCO ₃ ⁻ + H ⁺	-6.454
HCO ₃ ⁻ = CO ₃ ²⁻ + H ⁺	-10.159
HCO ₃ ⁻ + Na ⁺ = NaHCO ₃	-0.250
HCO ₃ ⁻ + Ca ²⁺ = CaHCO ₃ ⁺	1.450
HCO ₃ ⁻ + Mg ²⁺ = MgHCO ₃ ⁺	1.253
HCO ₃ ⁻ + Ba ²⁺ = BaHCO ₃ ⁺	2.268
HCO ₃ ⁻ + Sr ²⁺ = SrHCO ₃ ⁺	2.414
CO ₃ ²⁻ + Na ⁺ = NaCO ₃ ⁻	1.209
CO ₃ ²⁻ + Ca ²⁺ = CaCO ₃	3.716
CO ₃ ²⁻ + Mg ²⁺ = MgCO ₃	3.460
CO ₃ ²⁻ + Ba ²⁺ = BaCO ₃	2.851
CO ₃ ²⁻ + Sr ²⁺ = SrCO ₃	3.257
SO ₄ ²⁻ + Na ⁺ = NaSO ₄ ⁻	0.926
SO ₄ ²⁻ + K ⁺ = KSO ₄ ⁻	1.261
SO ₄ ²⁻ + Ca ²⁺ = CaSO ₄	2.666
SO ₄ ²⁻ + Mg ²⁺ = MgSO ₄	3.089
SO ₄ ²⁻ + Ba ²⁺ = BaSO ₄	2.216
SO ₄ ²⁻ + Sr ²⁺ = SrSO ₄	2.509

* H₂SO₄, HCl, NaOH, KOH, Ca(OH)₂, Mg(OH)₂, etc. are assumed to be completely dissociated.

TABLE 2. GAS-LIQUID EQUILIBRIA in HITEQ

	$K_H(100^\circ\text{C})$ (bars/molal)
$\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$	95.8
$\text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_3(\text{aq})$	0.3
$\text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{H}_2\text{S}(\text{aq})$	27.5
$\text{N}_2(\text{g}) \rightleftharpoons \text{N}_2(\text{aq})$	2278.8
$\text{O}_2(\text{g}) \rightleftharpoons \text{O}_2(\text{aq})$	1271.3

(BaCO_3), strontianite (SrCO_3), anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), barite (BaSO_4) and celestite (SrSO_4). The adopted solubility products K_{sp} (at 100°C) are shown in Table 3.

PREREINJECTION TREATMENT

Elsewhere, a scheme for silica removal from separated brines, based on increasing their pH, is discussed (Quong et al., 1978; Weres and Tsao, 1980). This change of pH may induce unwanted supersaturation of the brines with respect to other minerals such as calcite or witherite.

In order to assess the possible side effects of this silica removal scheme in Cerro Prieto brines, we used HITEQ to compute the chemical equilibrium of a representative brine (Table 4) and then varied the pH by adding H_2SO_4 and $\text{Ca}(\text{OH})_2$. The corresponding saturation ratios are presented in Figure 1. These results have been checked against computations kindly undertaken by D. L. Lessor at Battelle Northwest Laboratories, in an attempt to detect possible discrepancies. It was reassuring to find good agreement with the updated (September 1979 data base) version of Battelle's code.

Increasing the brine pH brings about potential scaling problems as indicated by the high

TABLE 3. MINERAL PHASES IN HITEQ

Mineral name	Chemical composition	$\log K_{sp}$ at 100°C
Calcite	CaCO_3	-9.495
Aragonite	CaCO_3	-9.334
Strontianite	SrCO_3	-11.973
Witherite	BaCO_3	-12.845
Anhydrite	CaSO_4	-5.165
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-5.106
Celestite	SrSO_4	-6.936
Barite	BaSO_4	-9.238

TABLE 4. AVERAGE BRINE COMPOSITION

Chemical	Concentration	
	ppm	molal
Na	6,610	0.288
K	1,436	0.037
Mg	1.2	0.00005
Ca	328	0.008
Sr	15.8	0.00018
Ba	11.3	0.000082
B	11	0.001
Cl	11,970	0.340
CO_2	44	0.001
SO_4^{2-}	9.6	0.0001
$\text{SiO}_2 \sim 500$ (1000)*		0.008 (0.016)
pH (100°C) = 7.35		

* In solution after (before) amorphous silica precipitation.

saturation ratios calculated for the carbonates. These problems can be circumvented by reducing the bicarbonate content of the brine before the

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Figure 1. Effects of adjusting pH on saturation ratios of carbonate and sulfate minerals for a typical separated Cerro Prieto brine.

silica removal treatment is applied. This can be accomplished by first decreasing the brine pH at intermediate pressures ($P_{\text{wellhead}} > P > 1 \text{ atm}$) thus inducing conversion of sizable amounts of solution bicarbonate into carbon dioxide, which then can be stripped from the solution by allowing the pressure to decrease and thereby causing further flashing. A possible implementation of this scheme is shown in Figure 2. The first separator pressure has been adopted according to current practices (Alonso et al., 1979).

Using HITEQ we find that the reconstructed brine at 6 bars and 159°C ($\text{SiO}_2 = 1000 \text{ ppm}$ before silica precipitation) has a pH of 7.02 and equilibrium ratios $\text{CO}_2:\text{HCO}_3^-:\text{CO}_3^{2-}::0.22:0.773:0.007$. Figure 3 shows the computed equilibrium shift when H_2SO_4 is added. At pH = 5 we find $\text{CO}_2:\text{HCO}_3^-::0.961:0.039$; 0.6 mmoles/kg of added H_2SO_4 were required to lower the pH to this value. We envision either no corrosion problems or minor ones at this moderate pH value. The computed saturation ratios in this condition, depicted in Figure 4, indicate that barite may be a limiting factor for use of inexpensive H_2SO_4 .

Flashing the acidified brine to $P \approx 1 \text{ bar}$ we compute pH = 6.34 and a liquid carbon content decreased to $3 \times 10^{-3} \text{ mmole/kg}$.

Increasing the pH of the separated brine by adding $\text{Ca}(\text{OH})_2$ we find the saturation ratios of Figure 5, which indicate that the proposed scheme can indeed control carbonate precipitation in treated Cerro Prieto brines. The amount of $\text{Ca}(\text{OH})_2$ necessary to increase the pH of the separated brine to ≈ 7.8 , as required by the silica removal treatment, was found to be about 0.5 mmole/kg. The brine is found to be supersaturated with respect to barite. This problem may be solved by replacing H_2SO_4 by HCl , though at higher cost.

Adopting 20 kg of separated brine per kWh we estimate that the treatment with H_2SO_4 will cost $2.0 \times 10^{-5} \text{ \$/kWh}$; using HCl instead we find a cost of $2.17 \times 10^{-4} \text{ \$/kWh}$. The cost of the lime treatment is merely $2.0 \times 10^{-5} \text{ \$/kWh}$. The prices of chemicals were taken from the

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Figure 2. Schematic of the proposed scheme of acid injection for inhibition of carbonate mineral deposition.

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Figure 3. Carbon dioxide partition in the first separator (P-bars) as a function of pH.

Chemical Marketing Reporter (January 21, 1980) as \$15/ton for tanks of smelter grade 100% H_2SO_4 ; \$62.50/ton for HCl 18° Baume (29% by weight HCl); and \$32.50/ton for CaO pebble. The acids prices are for the West Coast; the lime price is f.o.b.

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Figure 4. Effects of adding sulfuric acid on the saturation ratios of sulfate minerals (carbonate minerals out of scale) in the first separator.

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Figure 5. Effects of then adding calcium hydroxide on the saturation ratios of relevant minerals in the second separator (P-1 bar).

We conclude that the proposed scheme for the prereinjection brine treatment in Cerro Prieto is both technically and economically feasible. This tentative conclusion should be confirmed by experimental work due to uncertainties (e.g. validity of the Debye-Huckel approximation, values of the equilibrium constants) associated with the chemical model.

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