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Chemistry of Stibnite, Orpiment and Other Sulfide Minerals Deposited from Geothermal Brine

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ABSTRACT

Geothermal brines usually contain little arsenic, and even less antimony, iron, zinc or lead, but deposits containing stibnite (Sb_2S_3) or other sulfide minerals are sometimes encountered.

The solubility of sulfide minerals depend on the concentration of H_2S, as well as temperature and pH, whereby they behave differently from other, more common deposits from geothermal brines. In the case of stibnite and orpiment (As_2S_3), decreasing pH actually favors the formation of deposits. Deposits containing Sb, Pb and especially As pose threats to plant personnel and the environment due to their toxic nature.

Deposits of stibnite have been studied and described in connection with several geothermal plants in New Zealand, but otherwise the amount of industry experience and information related to chemistry of Sb, As, Fe, Zn and Pb in geothermal brines is quite limited. However, thermodynamic data sufficient to model the chemistry of these metals in geothermal power plants are available. The results of such modeling are presented here.

A representative brine of moderately challenging composition is put through several typical power generating cycles, allowing chemical behavior of Sb, As, Fe, Zn, Pb and other deposit-forming metals and metalloids to be compared. Stibnite and orpiment are the primary focus, but results related to other sulfide minerals and more common deposits including $CaCO_3$, aluminosilicates, silica, and Mg,Fe,Ca-silicates are also presented with reference to different power plant configurations.

1. INTRODUCTION

Deposits of antimony trisulfide (stibnite or "metastibnite") present serious problems at several geothermal power plants in New Zealand (Brown and Dorrington, 2001; Wilson et al., 2007; Brown, 2011) and are sometimes encountered in the United States, Turkey and elsewhere. Sometimes, deposits also containing arsenic are encountered (Brown, 2011). Successful removal of these deposits using solutions of NaOH has been reported (Brown and Dorrington, 2001; Lawson et al., 2018) and some scale inhibitors have shown useful effect (Muller et al., 2014).

Deposits of ZnS and PbS are also encountered. Iron generally precipitates together with Mg to form amorphous deposits of Mg,Fe,Ca-silicate composition, but complex sulfides which contain Fe together with other metals are sometimes reported.

Because deposits of Sb_2S_3 and As_2S_3 are quite different from other, more familiar deposits produced by geothermal brines, the published reports are largely limited to field observations. Brown (2011) briefly summarized computer modeling of Sb chemistry, but little else has been reported describing the chemical behavior of Sb and As in geothermal brines.

2. CALCULATIONS PERFORMED

2.1 Computer programs and data sources

The commercial computer program Geochemist's Workbench, Standard Edition, v 9.03 (GWB) was used to calculate the state of saturation of the brine in respect to minerals, and the precipitation of minerals from the brine which might occur unless inhibited.

The primary source of thermodynamic data used to model the brine was data file *speq06.dat* developed by the Lawrence Livermore National Laboratory, which is itself a derivative of *slop98.dat,* one of a series of serial data files used with SUPCRT92 (Johnson et al., 1992) compiled and released by the GEOPIG Group at Arizona State University. Improved data describing aqueous species and minerals of As, Sb, Ag, Au and Hg (Bessinger and Apps, 2003) were added along with other improvements. Finally, the serial data file was converted to direct access form using CPRONS92 (part of the SUPCRT92 package) and our proprietary data base *gpct06.dat* in GWB format was generated using DBCreate (Kong et al., 2014) with LLNL's data file *thermo.com.V8.R6+.dat* (which is distributed with GWB) serving as the template.

Our proprietary program NBRINE was used to calculate partitioning and transport of water, heat, H_2S and CO_2 in the steam separators and powerplant. The NBRINE program is derived from another program called CNDSR used to model the partitioning and transport of gases within the condensers and cooling tower of a geothermal powerplant (Weres, 1983; Weres, 1984).

2.2 The brine modeled

The composition of the geothermal brine modeled is presented in Table 1. This is a hypothetical brine which resembles many actual geothermal brines and was formulated to have moderately challenging chemical characteristics; most things known to precipitate from geothermal brines are predicted to precipitate from this model brine.

Temperature, alkalinity (represented by OH^-), and concentrations of Na, K, Fe, As, Sb, CO_2 and H_2S initially present in the brine were specified. Then, SiO_2, Ca, Mg, sulfate, Ba, Al, Zn and Pb were added to the brine in that order in the amounts needed to make the brine saturated in respect to quartz, calcite, dolomite, anhydrite, barite, anorthite, sphalerite and galena, respectively. These calculations were performed using GWB. The nominal chemical composition of the minerals discussed is presented in Table 2.

Moderately elevated concentrations of As, Sb and Fe were specified to ensure that deposits containing these elements would result. The concentrations of As and Sb specified are much lower than would make the brine saturated with respect to orpiment and stibnite at 240ºC; this is consistent with the observation that orpiment and stibnite are rare minerals. The initial concentration of Fe is 2,000 times greater than would be present in equilibrium with pyrite, but is in the range of Fe commonly added to a geothermal brine by corrosion of the production well casing, etc.

Table 1. Initial composition of the brine modeled

Concentration in mg-moles / kg-H_2O as input to Geochemists' Workbench

Parameter / Ion			
T(ºC)	240	Assumed	
H_2O (kg)	1.0		
pH at T	5.89	Calculated	
	mg-moles / kg-H_2O	mg / kg-brine	
Na^+	180.	4,081.	Concentration assumed
K^+	20.	771.	
OH^- (a)	1.0	–	
CO_2 (b)	25.0 (c)	–	
H_2S (c)	1.0 (d)	–	
Fe^{+2} (d)	0.0086	0.48	
$As(OH)_3$	0.06	4.43 as As	
$Sb(OH)_3$	0.006	0.73 as Sb	
(e)	Concentration calculated based on solubility of		
SiO_2	6.98	414.	Quartz
Ca^{+2}	3.45	136.	Calcite
Mg^{+2}	0.05	1.20	Dolomite
SO_4^{-2}	1.11	105.	Anhydrite
Ba^{+2}	0.0165	2.24	Barite
$Al(OH)_4^-$	0.0257	0.68 as Al	Anorthite
Zn^{+2} (f)	30.5 ng-mol	0.00196	Sphalerite
Pb^{+2} (f)	33.8 ng-mol	0.00691	Galena
Cl^-	203.8	7125.	Charge Balance

(a) Represents measured alkalinity.

(b) Total CO_2 which includes HCO_3^- and CO_3^{-2} together with CO_2 (aq) and complexes of these ions.

(c) Concentration of total H_2S, which includes HS^- together with H_2S (aq) and sulfide complexes.

(d) Represents Fe added to the brine by corrosion of the well casing; about 2,000 greater than the solubility of pyrite (FeS_2) under these conditions.

(e) Remaining ions "added" to the brine in the order indicated.

(f) Equilibrium concentrations of Zn and Pb in nanogram-mol = 10^{-9} mol / kg-H_2O.

Table 2. Minerals assumed present in reservoir or potentially precipitated

The nominal chemical composition tabulated for each mineral is that used by Geochemist's Workbench to model the solubility of that mineral.

Mineral	Nominal Composition	
Anhydrite	$CaSO_4$	Assumed present in Reservoir
Anorthite	$CaAl_2Si_2O_8$	
Dolomite	$CaMg(CO_3)_2$	
Quartz	SiO_2	
Barite	$BaSO_4$	Assumed present in Reservoir and Potentially Precipitated
Calcite	$CaCO_3$	
Galena	PbS	
Sphalerite	ZnS	
Amorphous silica	SiO_2	Potentially Precipitated
Clinoptilolite–K	$K_{1.1}Al_{1.1}Si_{4.9}O_{12}\cdot 2.7H_2O$	
Orpiment	As_2S_3	
Stibnite	Sb_2S_3	
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	
Berthierite	$FeSb_2S_4$	Potentially Precipitated if Fe is present in the Brine
Pyrrhotite	FeS	
Minnesotaite	$Fe_3Si_4O_{10}(OH)_2$	

2.3 Power generating systems modeled

Figures 1 and 2 on the following page illustrate the two systems modeled using the NBRINE program. These models actually represent a total of six distinct power cycles running on the same geothermal brine. The "boxes" in the model that discharge the brine leaving each power cycle are:

1. Simple pumped binary (HEX1 in Figure 1).
2. Single stage flash (HPSEP).
3. Single stage flash with binary bottoming unit (HEX2).
4. Two stage flash (LPSEP).
5. Two stage flash with binary bottoming unit (HEX3).
6. High temperature binary receiving two phase fluid (MIX and HEX4 in Figure 2).

The temperature of brine leaving the heat exchangers was set to 65ºC, which is typical of the value specified for binary and combined cycle geothermal power plants.

3. CALCULATED RESULTS

The amount of each mineral potentially precipitated, and difference between the power cycles considered are summarized in Table 3. The temperature at which the brine becomes supersaturated with respect to each mineral is given in Table 4. The four minerals in Part A of the Table have normal solubility; that is, solubility increases with temperature, and the mineral may precipitate below the temperature indicated. The four minerals in Part B have retrograde solubility; that is, solubility decreases with temperature, and the mineral may precipitate above the temperature indicated.

The metal silicate deposits produced by geothermal brines usually are amorphous (rarely, well defined clay minerals are identified). When GWB predicts that a metal silicate mineral will precipitate, this really means that an amorphous material of similar composition is likely to form.

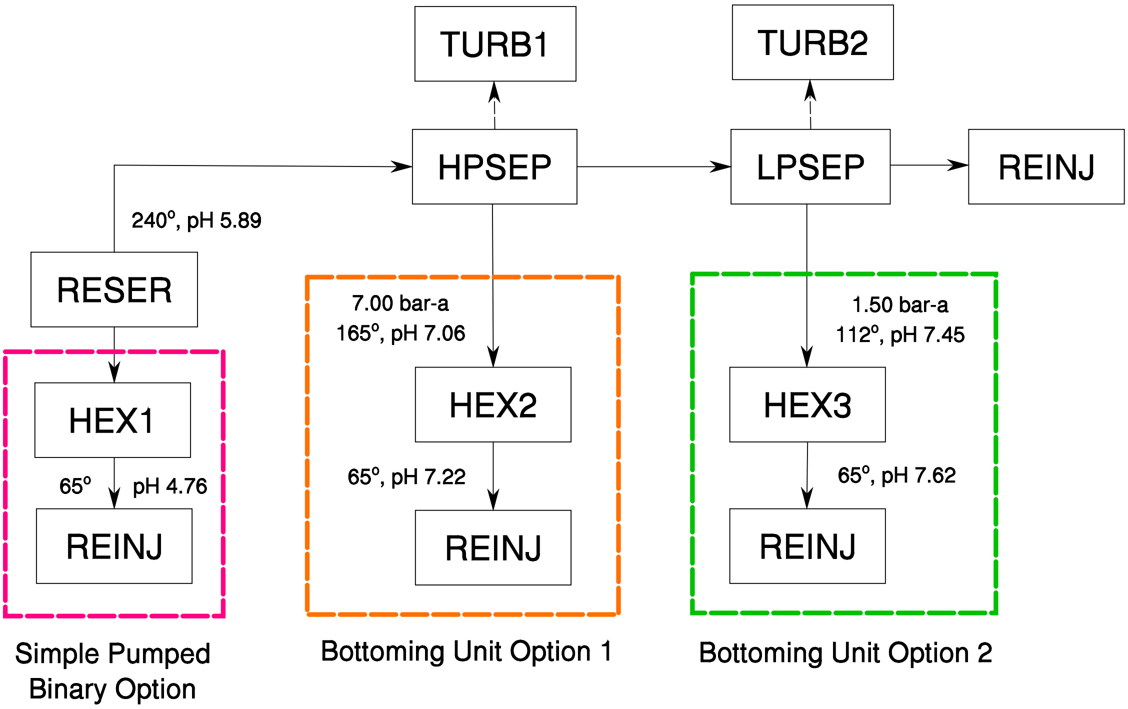

Figure 1. One simple binary, two flashed steam, and two combined power cycles modeled using NBRINE.

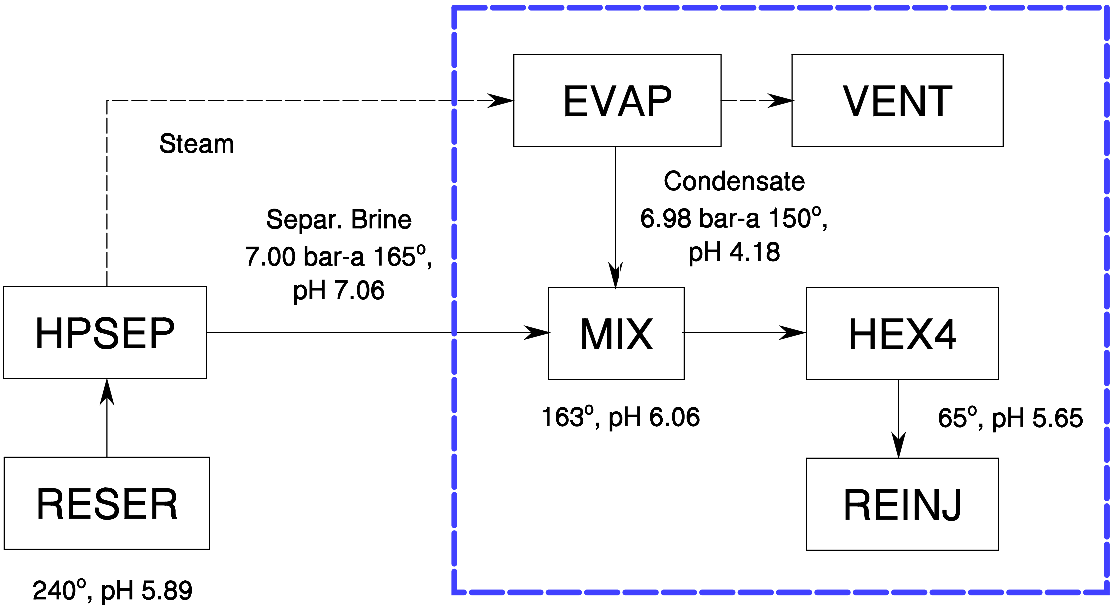

Figure 2. High temperature binary cycle as modeled using NBRINE.

3.1 Iron sulfides

The concentration of Fe naturally present in geothermal brine usually is vanishingly small, because the solubility of pyrite is very small in the presence of H_2S. However, corrosion of the well casing, etc., adds some Fe to the brine. As a result, produced geothermal brines commonly are highly supersaturated in respect to pyrite, but pyrite does not precipitate, because formation of pyrite requires a change of oxidation state, which is a slow reaction.

Iron usually precipitates together with Mg, forming an amorphous silicate deposit which also contains some Ca. However, FeS may precipitate if the concentration of H_2S is high, and Fe sometimes precipitates forming complex sulfides that also contain other metals (Sect. 3.4 below).

Table 3. Minerals potentially precipitated.

Part A	HEX1	HPSEP	HEX2	LPSEP	HEX3	MIX	HEX4
T(°C)	65	165	65	112	65	163	65
H_2O (kg) (a)	1.0	0.8388	0.8388	0.7539	0.7539	0.9993	0.9993
Total CO_2 (b)	25.0	0.698	0.698	0.265	0.265	3.86	3.86
Total H_2S (b)	1.0	0.0992	0.0992	0.0173	0.0173	0.403	0.403
pH at T	4.76	7.05	7.20	7.45	7.62	6.06	5.65
Part B (c)	Amount potentially precipitated (mg/kg-H_2O in reservoir brine)						
Amorphous SiO_2 (d)	179.	0	204.	50.	199.	0	179.
Barite (e)	2.61	1.38	2.83	2.09	2.94	0.92	2.62
Calcite	0	12.4	0	1.62	0	0	0
Clinoptilolite-K	10.5	10.5	10.5	10.5	10.5	10.5	10.5
Minnesotaite	0	1.35	0.87	1.35	0	1.25	0
Tremolite	0	8.07	1.82	8.10	7.72	0.28	0
Part C (c,e)	Sulfide minerals potentially precipitated (mg/kg-H_2O in reservoir brine)						
Berthierite	0	0	1.26	0	0	0	1.27
Galena	0.0080	0.0080	0.0081	0.0081	0.0081	0.0075	0.0081
Orpiment	7.08	0	0	0	0	0	6.39
Sphalerite	0.0030	0.0029	0.0030	0.0030	0.0030	0.0029	0.0030
Stibnite	1.01	0	0	0	0.84	0	0
If no Fe in brine	1.01		0.99		0.84		1.01

(a) Amount of water remaining per kg H_2O in reservoir brine.

(b) Units are (mg-mol / kg–H_2O) in reservoir brine.

(c) The amount of solids potentially precipitated at each stage calculated assuming that (i) no solids precipitated at any earlier stage, and (ii) precipitation reached chemical equilibrium at this stage. Therefore, the values in the columns cannot be added across the table.

(d) The amount of amorphous silica actually precipitated usually is a fraction of the amount potentially precipitated.

(e) The amounts of other minerals potentially precipitated were calculated assuming that no amorphous SiO_2 precipitates, because amorphous SiO_2 precipitates much more slowly. Prediction of crystalline metal silicate minerals (clinoptilolite, tremolite, minnesotaite) actually indicates precipitation of amorphous solids of similar composition.

3.2 Galena and Sphalerite

Solubility and precipitation of galena (PbS) and sphalerite (ZnS) are controlled by temperature, the presence of H_2S, and pH. For example:

$$Zn^{+2} + H_2S + 2\ OH^- \Rightarrow ZnS(s) + 2\ H_2O \qquad (1)$$

Separating steam strips H_2S from the brine while also increasing pH, which has the opposite effect upon solubility; these two effects partly cancel out, with the result that the solubility and precipitation of these minerals is largely controlled by temperature.

Nearly complete precipitation of Zn and Pb as sphalerite and galena is predicted in all cases modeled. However, deposits of these minerals are rarely reported because the concentration of Zn and Pb in geothermal brines usually is very small.

Table 4. Temperature at which brine becomes saturated.

These temperature values are calculated assuming that nothing precipitates.

	RESER	HPSEP	LPSEP	MIX
Part A	Mineral may precipitate when T is below this value			
Amorphous SiO_2	108	120	125	108
Berthierite	187	139	100	176
Orpiment	104	50	17	87
Stibnite	173	112	82	152
Part B	Mineral may precipitate when T is above this value			
Calcite	240	101	92	190
Minnesotaite	183	< 0	< 0	117
Pyrrhotite	172	< 0	< 0	101
Tremolite	218	57	24	161

3.3 Antimony trisulfide (stibnite or "metastibnite")

Results related to solubility and precipitation of minerals containing Sb and As are presented in Table 3, Part C, and Table 5, Part B. Speciation of Sb in solution is described in Table 5, Part C.

Usually, Sb precipitates from geothermal brine as Sb_2S_3. At the lower temperature leaving a heat exchanger, the deposits produced are amorphous, red or orange "metastibnite"; at high temperature the black mineral stibnite is sometimes produced (Muller et al., 2014).

At high temperature, Sb is present in solution mostly as $Sb(OH)_3$ and the reaction producing stibnite is

$$2\ Sb(OH)_3 + 3\ H_2S \Rightarrow Sb_2S_3 + 6\ H_2O \qquad (2)$$

The equilibrium constant for this reaction, calculated using SUPCRT92 and thermodynamic parameters provided by Bessinger and Apps (2005), is reproduced up to 250ºC by the formula

$$\mathrm{Log}_{10}\ K = 47.09 + 10915\ /\ T(K) - 19.636\ \mathrm{Log}_{10}\ T(K) \qquad (3)$$

where T(K) = T(ºC) + 273.15 and the third term accounts for the fact that the chemical reaction changes the heat capacity of the system as well as the entropy and enthalpy.

Brine initially containing 0.006 mg-mol/kg Sb (0.73 ppm) is far from saturation with stibnite in the reservoir or leaving HPSEP and LPSEP. In each case, the amount of Sb needed to precipitate stibnite would be far greater than ever reported in a geothermal brine (Table 5, Part B). Adding condensate from EVAP to the brine leaving HPSEP increases the amount of H_2S four-fold in MIX, bringing the brine closer to saturation; even here, Sb > 1.75 mg /kg-H_2O would be needed to precipitate stibnite.

It is sometimes stated that adding condensate to brine induces stibnite to precipitate by decreasing pH (Wilson et al., 2007; Brown, 2011). Indeed, reaction (3) requires H_2S rather than HS^-, and decreasing pH converts HS^- to H_2S. However, the effect of increased H_2S concentration is more important. The effect of adding condensate from EVAP to the brine from HPSEP can be summarized as follows (amounts in mg-moles/kg-H_2O in reservoir brine):

HPSEP (pH 7.05) + EVAP (pH 4.18) ⇨ MIX (pH 6.06)

$$(0.017\ H_2S + 0.082\ HS^- + 0.048\ HCO_3^-) + 0.304\ H_2S \Rightarrow 0.273\ H_2S + 0.130\ HS^- + 0.048\ CO_2$$

The amount of HS^- in MIX is slightly larger than in HPSEP, despite lower pH, but the amount of H_2S is much larger, increasing the saturation index S for stibnite and favoring precipitation when the temperature drops inside HEX4.

The situation at 65ºC is different. The hydroxide species $Sb(OH)_3$ predominates only in LPSEP where the amount of H_2S is very small. In the presence of H_2S (HEX1, HEX2 and HEX4), Sb is present mostly as the sulfide complexes $H_2Sb_2S_4$ and $HSb_2S_4^-$ (Table 5, Part C). Formation of these complex species greatly increases the solubility of stibnite at low temperature by keeping Sb in solution. In the absence of these complexes, the concentration of Sb at equilibrium with stibnite in MIX would be only 0.037 ppb, rather than 0.086 ppm (86 ppb) reported in Table 5, Part B.

While adding H_2S to the brine at high T favors precipitation of Stibnite by promoting reaction (2), at low T H_2S also inhibits precipitation by keeping Sb in solution as the sulfide complexes. These effects practically cancel out, whereby the greater amount of

H_2S in HEX1 and HEX4 has only a small negative effect upon the solubility of stibnite as compared to HEX2 and HEX3. This means that precipitation of stibnite from brine leaving a heat exchanger will mostly be controlled by the concentration of Sb and temperature, while the concentration of H_2S (assuming that some H_2S is present) has less effect.

The big effect of temperature upon speciation of Sb is consistent with modeling reported by Brown (2001) who reported that $Sb(OH)_{3(aq)}$ is predominant at 150ºC, while $HSb_2S_4^{--}$ predominates at 25ºC.

In contrast to amorphous silica, deposits of Sb_2S_3 cannot easily be controlled by adjusting the temperature of brine leaving the heat exchanger. The brine flowing through heat exchangers HEX1, HEX2, HEX3 and HEX4 become supersaturated with respect to stibnite at 173°, 112°, 82° and 152ºC, respectively (Table 4).

When Sb_2S_3 precipitates from geothermal brine at lower temperature leaving a heat exchanger, the deposit is red or orange "metastibnite", an amorphous, metastable material which is more soluble than stibnite (Brown, 2011; Muller et al., 2014). Observations by Powerchem personnel in the United States and Turkey confirm these reports from New Zealand: deposits of Sb_2S_3 in binary bottoming units and pipelines leading to injection wells are red or orange rather than black, the color of stibnite.

The thermodynamic properties of stibnite are well defined, and solubility can be calculated with reasonable accuracy. However, prediction of Sb_2S_3 deposits based on solubility of stibnite are necessarily pessimistic, because precipitation of red Sb_2S_3 requires higher concentrations of Sb than calculated here, assuming that stibnite actually precipitates. In fact, precipitation of Sb_2S_3 would begin at an Sb concentration somewhat higher than the values calculated and presented in Table 5, Part B.

3.4 Complex sulfides containing antimony along with other metals

Antimony also occurs in a variety of complex sulfide minerals which contain other metals, in addition to Sb. Such complex Sb-sulfides are sometimes identified in deposits from geothermal brines. Bessinger and Apps (2005) provided thermodynamic parameters describing one such mineral, berthierite, with the composition $FeSb_2S_4$.

The 0.48 ppm Fe initially present in the brine modeled suffices to induce precipitation of berthierite from brine leaving HEX2 and HEX4. The brine leaving HEX1 and HEX3 is also supersaturated in respect to berthierite, but precipitation of stibnite is favored.

3.5 Arsenic trisulfide (Orpiment)

The chemical behavior of As in geothermal brines is generally similar to Sb with one major difference; As_2S_3 is much more soluble than Sb_2S_3. Although the molal concentration of As in the brine modeled is 10 times greater than the concentration of Sb (0.06 mg-mol/kg vs. 0.006 mg-mol/kg; Table 1), orpiment is predicted to precipitate only from the brines containing a substantial amount of H_2S, and only at low temperature (HEX1 and HEX4 at 65ºC, Table 3, Part C).

Similar to Sb, the hydroxide complex $As(OH)_3$ is the major aqueous species at high temperature. Unlike Sb, a significant fraction of the $As(OH)_3$ dissociates, forming the anion $As(OH)_4^-$, thereby increasing the solubility of orpiment, which is controlled by the reaction

$$2\ As(OH)_3 + 3\ H_2S \Rightarrow As_2S_3 + 6\ H_2O \qquad (4)$$

The equilibrium constant for this reaction, calculated using SUPCRT92 and thermodynamic parameters provided by Bessinger and Apps (2005), is reproduced up to 250ºC by the formula

$$\mathrm{Log}_{10}\ K = 69.62 + 7245 / T(K) - 27.647\ \mathrm{Log}_{10}\ T(K) \qquad (5)$$

Similar to Sb, sulfide complexes of As become important at low temperature if H_2S is present, but not as much as with Sb; $As(OH)_3$ is still the major species coming out of HEX4, and significant in the brine leaving HEX1. Therefore, the effect of sulfide complexes increasing the solubility of orpiment is significant at low temperature, but less so than with stibnite.

4. OPTIONS FOR CONTROLLING DEPOSITS OF STIBNITE AND ORPIMENT

At high temperature, leaving a steam separator or entering a heat exchanger, the solubility of Sb_2S_3 is controlled by the concentration of H_2S in the brine, and to a lesser degree by pH, with determines the equilibrium between H_2S and HS^-. In power cycle configurations where steam condensate in returned to the brine, reducing the amount of H_2S returned with the condensate will delay deposits of Sb_2S_3 entering the heat exchanger.

However, at low temperature, exiting a heat exchanger, most of the Sb is tied up as sulfide complexes. As noted in Section 3.3, formation of sulfide complexes greatly reduces the effect of H_2S concentration upon solubility of Sb_2S_3. Therefore, decreasing the concentration of H_2S in the brine would be of little benefit in controlling deposits leaving the heat exchanger or in the brine disposal system. Similarly, increasing terminal temperature would provide little benefit, because precipitation of Sb_2S_3 inside the heat exchanger begins well above typical terminal temperature (Table 4).

Because the concentration of H_2S, temperature and pH have limited effects upon the solubility of Sb_2S_3 at low temperature, solubility and deposits of Sb_2S_3 are mostly controlled by the concentration of Sb in the brine, a parameter over which the plant operator has no control. This conclusion leaves just two practical options for controlling Sb_2S_3 deposits in the low temperature part of a heat exchanger and brine reinjection system: chemical inhibitors, or removing the deposits that form. Success has been reported controlling deposits of Sb_2S_3 using products of the kind commonly used to control metal silicate deposits (Muller et al., 2014). Powerchem has also used conventional scale inhibitors to control Sb_2S_3 with some success.

The behavior of As_2S_3 is generally similar to Sb_2S_3. Fortunately, highly toxic As_2S_3 is rarely encountered because it is much more soluble than Sb_2S_3. Because As is less prone to form sulfide complexes at low temperature, limiting the concentration of H_2S in brine entering the heat exchanger may be a viable control option. If the H_2S concentration is small and $As(OH)_{3(aq)}$ is the major form of As in solution, increasing pH might also be considered to inhibit As_2S_3.

Table 5. Solubility and speciation of Sb and As

(a) 1 µg-mol = 10^{-6} g-mol. A blank in Part C or D indicates concentration < 0.01 µg-mol/kg-H_2O.

Part A		RESER	HEX1	HPSEP	HEX2	LPSEP	HEX3	MIX	HEX4
T(℃)		240	65	165	65	112	65	163	65
H_2O (kg)		1.0	1.0	0.8388	0.8388	0.7539	0.7539	0.9993	0.9993
Total H_2S		1.0	1.0	0.0992	0.0992	0.0173	0.0173	0.403	0.403
pH at T		5.89	4.76	7.05	7.20	7.45	7.62	6.06	5.65
Part B		Solubility expressed as concentration of Sb, As or Fe (mg/kg-H_2O reservoir brine)							
Berthierite	Sb	> 23	0.24	6.8	0.0092	2.55	0.39	0.28	0.063
Minnesotatite	Fe	0.027	> 4.8	0.0006	0.0054	0.00027	0.73	0.037	> 4.8
Orpiment	As	> 142	1.31	> 142	28	> 142	> 142	> 142	1.59
Pyrrhotite	Fe	0.032	32	0.014	0.021	0.036	38	0.055	1.73
Stibnite	Sb	> 23	0.077	> 23	0.115	22	0.114	1.75	0.086
Part C	(a)	Concentration of Antimony Species (µg-mol/kg-H_2O in brine)							
$Sb(OH)_3$		6.0	–	7.1	0.14	7.9	6.3	5.8	–
$Sb(OH)_4^{-}$		–	–	0.014	–	0.018	–	–	–
$H_2Sb_2S_4$		–	1.65	–	0.014	–	–	–	0.41
$HSb_2S_4^{-}$		–	1.35	–	3.2	–	0.66	0.066	2.6
$Sb_2S_4^{-2}$		–	–	–	0.32	–	0.18	–	–
Part D	(a)	Concentration of Arsenic Species (µg-mol/kg-H_2O in brine)							
$As(OH)_3$		56	3.7	50	68	59	70	58	18
$As(OH)_4^{-}$		4.5	–	21	3.6	21	9.9	2.35	0.026
$H_3As_3S_6$		–	0.36	–	–	–	–	–	0.035
$H_2As_3S_6^{-}$		–	18.3	–	–	–	–	–	13.4
$HAs_3S_6^{-2}$		–	0.13	–	–	–	–	–	0.71

5. SUMMARY AND CONCLUSIONS

The results presented here illustrate how the chemical behavior of geothermal brine can be modeled at all stages of the power generation process, producing useful results consistent with observations at geothermal powerplants. The processes controlling formation of deposits of Sb_2S_3 and Sb_2S_3, and other sulfides, are different from other, more familiar deposits, but the chemistry of Sb and As in geothermal brines can now be usefully explained and predicted.

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