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Antimony and Arsenic Sulfide Scaling in Geothermal Binary Plants

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ABSTRACT

With the advent of acid dosing for silica scaling control, and the increased utilisation of binary plants, the incidence of antimony sulphide scaling has become a concern. To a much lesser extent, arsenic sulphide scaling can also occur under similar circumstances. The combination of lower brine temperatures and lower pH can lead to significant antimony sulphide scaling. Although the antimony concentration in the brine can be very low, antimony sulphide scaling can become almost quantitative. This can lead to loss of heat transfer in binary plant heat exchangers, and injectivity decline in reinjection wells. Recent work has produced averaged thermodynamic data that seems to better predict the onset of stibnite scaling. Present options for remediation include caustic soda washing, steam cleaning and mechanical removal.

1. INTRODUCTION

With the increasing demand for electricity, the use of binary generation for bottoming plants is increasing. As well, binary plants are receiving more attention for development of lower temperature resources and even for higher temperature resources where maintenance of reservoir fluid volume is important.

Geothermal reservoir fluids often contain small concentrations of antimony and normally greater, but still small concentrations of arsenic. Binary plants often have lower brine temperatures than conventional flash plants. Moreover, due to either pH modification, or addition of condensate, the brine can have low pH. Under these conditions, antimony(III) sulfide (stibnite) can precipitate in the heat exchangers and cause a loss of heat transfer and can eventually block the heat exchanger tubes.

Stibnite has also been observed in conventional flash plants where brine is subjected to pH modification followed by cooling to lower temperatures – for instance where cooled water is required for pH measurement.

Although arsenic sulfide has higher solubility than antimony sulfide, at low temperatures arsenic(III) sulfide can also precipitate and cause the same problems as stibnite.

Re-evaluation of the thermodynamic data has led to more accurate data for stibnite equilibrium thermodynamics and has been verified in a geothermal binary plant.

2. THERMODYNAMICS OF ARSENIC SULFIDE AND ANTIMONY SULFIDE

2.1 Antimony

Stibnite is antimony(III) sulphide Sb_2S_3. It occurs naturally as a mineral that normally forms acicular (long, needle-like) black crystals. Like arsenic, antimony has two oxidation states Sb^{3+} and Sb^{5+}. Thus stibnite has antimony in the reduced oxidation state of +3. Crystalline stibnite is soft (mohs hardness = 2), and has a density of 4.63 g/ml. The melting point is 550ºC.

Sb_2S_3 also occurs as metastibnite. This is the amorphous analogue of crystalline stibnite. When stibnite is formed rapidly, for instance if a concentrated alkaline solution is acidified, then metastibnite is often formed. Metastibnite is an amorphous (non-crystalline) colloid and is red coloured.

Stibnite dissolves in water to form the “hydroxide” $Sb(OH)_3$ given by:

$$Sb_2S_3 + 6\,H_2O = 2\,Sb(OH)_3 + 3\,H_2S$$

However, this “hydroxide” behaves more like an acid, so it is often written as H_3SbO_3 which is called antimonous acid. It can dissociate to form an anion (negatively charged species) according to:

$$H_3SbO_3 = H_2SbO_3^- + H^+$$

which is sometimes also written as:

$$H_3SbO_3 + H_2O = H_4SbO_4^- + H^+$$

The species $H_4SbO_4^-$ is also sometimes written as $Sb(OH)_4^-$. The pK for this reaction is 12.04 at 25ºC, which means that at a pH of ~ 12 at 25ºC, there is approximately equal concentrations of H_3SbO_3 and $H_2SbO_3^-$. As the pH is increased, more of the H_3SbO_3 is converted to the anion. As the anion $H_2SbO_3^-$ is charged, it has a very high solubility in water. This is the basis for adding caustic soda to dissolve the stibnite.

A number of other complexes of Sb(III) have been proposed that are also based on the antimony hydroxide such as $Sb(OH)_2^+$ and $Sb(OH)_2F$. Antimony does not occur as the free ion (Sb^{3+}) except in very acid conditions.

However, in solutions where H_2S is present, stibnite can also dissolve to form sulfosalts of antimony:

$$Sb_2S_3 + H_2S = H_2Sb_2S_4$$

These thioantimonites dissociate in alkaline solutions to form the anions of the thioantimonites:

$$H_2Sb_2S_4 = HSb_2S_4^- + H^+$$

and $$HSb_2S_4^- = Sb_2S_4^= + H^+$$

These thioantimonites are only significant where the H_2S concentrations are significantly large or when the temperature is lower with H_2S present. They are, however, more stable than their arsenic analogues.

Antimony also exists in oxidised +5 forms. There is a slow oxidation in air for Sb(III) compounds and eventually the oxidised Sb(V) species is formed as $Sb(OH)_6^-$. The effect of bacteria on this oxidation has not been studied. However, in geothermal brines, Sb(III) is the oxidation state.

Antimony also exists in a (-3) oxidation state in the gas stibine SbH_3. This compound is extremely toxic and can be formed by the action of acid on antimony compounds in the presence of reducing compounds – like zinc. It has a similar smell to H_2S, so can be hard to detect in geothermal situations.

There is still some disagreement in the literature about the exact nature of all of the antimony complexes, and it is not currently a large area of research. Although there is a large amount of data on arsenic complexes, the literature is rather lean on antimony complexes.

2.2 Arsenic

Arsenic is also present in geothermal brines as the reduced As(III) form. Like antimony, it does not occur as discrete As3+ ions in solution, but as H_3AsO_3. Like antimony, this can also dissociate in alkaline solutions to form $H_2AsO_3^-$. The pK_1 and pK_2 for arsenites are 9.23 and 12.13 at 25ºC, so the arsenious acid H_3AsO_3 is the stable species at geothermal pH.

Also, in a similar manner to antimony, arsenic in the presence of H_2S can form thioarsenites such as $H_3As_3S_6$, $H_2As_3S_6^-$ and $HAs_3S_6^=$.

Arsenic also exists in an oxidised +5 state as arsenic acid H_3AsO_4. The pKs for dissociation of arsenates are 2.2, 6.97 and 11.53 at 25ºC, and so the species $H_2AsO_4^-$ and $HAsO_4^=$ are the stable species at normal pH. Arsenic (III) is oxidised to As(V) slowly in air, but experiments in the Wairakei geothermal drains have shown that this reaction rate is significantly increased where bacteria are present.

Arsenic also exists in a -3 oxidation state in the gas arsine AsH_3. It is also very toxic.

3. ANTIMONY SULFIDE IN GEOTHERMAL DEVELOPMENT

Antimony sulfide solubility is very sensitive to temperature and pH changes. The operation of some binary plants can encounter both lower pH and low temperature. Specifically, where steam is condensed in a vaporizer and then is added to the brine, and then led to a preheater, there is the opportunity for low temperature and low pH. It is mainly under these conditions that stibnite has been deposited in binary plants in New Zealand.

Antimony concentrations in geothermal brine are typically less than the arsenic concentrations – sometimes an order of magnitude less. However, it is normally stibnite that is observed in binary plant preheaters. Typical antimony concentrations are < 1 ppm, but calculations show that it can be almost quantitatively deposited as stibnite. If we consider just the reaction:

$$Sb_2S_3 + 6H_2O = 2H_3SbO_3 + 3H_2S$$

then calculations of the solubility of stibnite as ppm Sb as a function of pH, temperature and H_2S concentration is as follows:

	pH = 5	pH = 5	pH = 8	pH = 8
temp	5ppm H2S	15 ppm H2S	5ppm H2S	15 ppm H2S
25	6.50E-08	1.24E-08	2.51E-06	4.83E-07
50	4.91E-06	9.37E-07	4.32E-04	8.32E-05
100	7.97E-03	1.52E-03	1.01	0.19
150	3.34	0.637	224	43
200	446	85	9852	1897

As can be seen, there is a very large temperature effect, with stibnite solubility decreasing by 2 -3 orders of magnitude with a 50ºC drop in temperature, and also a large pH effect with 2-3 orders of magnitude drop in solubility between pH = 8 and pH = 5.

The speciation of the antimony in solution is also affected by temperature and pH. As an example, a brine with H_2S = 10 ppm and Sb = 0.2 ppm has the following calculated speciation at different temperatures and pH. The speciation is given in ppb of contained Sb for comparison.

Temp ºC	pH	$Sb(OH)_3$	$HSb_2S_4^-$
25	5	0.02	200
150	5	194	6.49
25	7	0.01	200
150	7	198	1.48
25	8	0.09	200
150	8	198	0.00

There are also very small amounts of other antimony species present.

In binary plants, the stibnite is precipitated usually as the black crystalline form, rather than the red amorphous form. The crystals are acicular – long thin needles (Figure 1). These needles pack loosely on the heat exchanger pipe surface and form a very porous layer that can trap brine. The needles, plus the trapped brine can reduce the heat transfer in the heat exchanger. As well, the silica in the brine that is trapped in the pore spaces can polymerise and deposit. This can change the scale from a soft, easily removed scale to one more difficult to remove mechanically.

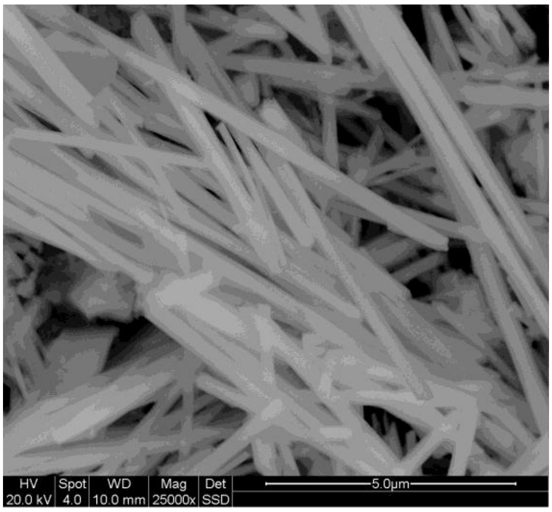

Figure 1: Stibnite crystals

Where the stibnite is precipitated quickly – for instance by acidifying a caustic solution, it deposits as the red amorphous compound (Figure 2).

Figure 2: Amorphous antimony sulfide

Originally, it was thought that stibnite might be volatile and could precipitate in steam lines. However, no evidence has been found that stibnite is distributed into the vapour phase.

3.1 Stibnite Mitigation in Binary Plants

A number of possibilities exist for mitigating the deposition of stibnite. However, some are either not practical or not economic options.

3.1.1 Avoidance of low temperature

If the brine temperature is maintained above the saturation temperature for stibnite, then deposition cannot occur. This is generally not a practical solution as there can be a considerable loss of power generation.

3.1.2 Avoidance of low pH

The low pH that occurs in binary plants is normally due to the low pH condensate being added to the neutral brine. If these two streams are kept separate, then stibnite deposition is normally unlikely to occur. The acidity in the condensate is due to dissolved gases. If these gases could be purged, then perhaps they could be mixed with brine prior to the preheater without causing stibnite deposition.

3.1.3 Caustic dosing

Either the condensate or the mixed brine could be dosed with caustic to raise the pH. The required pH can be calculated, but is normally not that high. However, caustic is expensive, and this method normally is not economically viable.

3.1.4 Chemical inhibition

It may be possible to develop an antiscalant in a similar manner to the use of calcite antiscalants. Some research has been carried out in this area, but as yet, there are no antiscalants on the market that have been shown to be successful in inhibiting stibnite deposition. However, research is continuing.

3.1.5 Mechanical removal

If no preventative measures appear to be practical, then periodic removal of the deposit becomes the only option. High pressure water blasting using specialist rotating tube cleaning heads was found to be partially successful, but found to be expensive, slow and messy. The latter is important as stibnite is a hazardous material.

Later, specialised water flushed drilling equipment was employed and this proved to be very effective but still very time consuming. The time factor is also important, as this is a loss of power production.

3.1.6 Chemical removal

This is the method that is employed to date most successfully in New Zealand. (eg Dorrington and Brown, 2000). Hot caustic soda is recirculated through the heat exchangers and the stibnite is dissolved very quickly. If silica is co-precipitated, then it also tends to be dislodged, but not necessarily dissolved. Cleaning an individual machine can be accomplished relatively quickly – a few hours – and loss of production is minimized. It is advisable to carry out this cleaning regularly. If heat exchanger tubes become blocked, then the caustic solution cannot pass through and incomplete cleaning is observed.

A second possibility is to divert the brine from the heat exchangers and just pass steam through the vaporizer and then the preheater. Without the brine, the stibnite slowly dissolves and can be led to reinjection. This method has the advantage that (possibly reduced) power production is possible during the cleaning.

4. ARSENIC SULFIDE IN GEOTHERMAL DEVELOPMENT

Arsenic sulfide behaves in a similar manner to antimony sulfide. However, arsenic sulfide is less commonly observed, despite the fact that arsenic concentrations are normally a magnitude greater than antimony concentrations.

Recent experiments have shown that an amorphous arsenic sulfide can be precipitated at low pH and very low temperature. Consequently, although arsenic behaves in a similar manner to antimony, the saturation temperature and pH seem to be lower.

5. SAMPLING FOR ANTIMONY AND ARSENIC

Traditionally, brine samples for antimony and arsenic analysis have been collected as filtered, acidified samples. However, the thermodynamics suggest that both arsenic and antimony would be better preserved in alkali. When this was tested on brine from a geothermal development, the following results were obtained. Concentrations of arsenic and antimony shown are in ppb:

	Preservative	Arsenic	Antimony
Accumulator	Acid	71	8
	Alkali	1850	426
Reinjection line	Acid	51	< 2
	Alkali	1230	165
Ultra pure water	Acid	< 10	< 2
	Alkali	< 10	< 2

From these results, it is clear that preservation with caustic is advisable for antimony and arsenic analysis.

A further problem arises with the cooling coils used for sampling brine at > 100ºC. If the residence time in the cooling coil is large, then stibnite can be deposited in the coil or stibnite crystals carried in the brine flow and then further analytical errors are seen.

Consequently, it is sometimes quite difficult to obtain reproducible analyses for these elements. .

6. THERMODYNAMIC DATA

The thermodynamic data for the reaction:

$$0.5\ Sb_2S_{3(s)} + 3\ H_2O_{(l)} \leftrightarrows Sb(OH)_{3(aq)} + 1.5\ H_2S_{(aq)}$$

have been investigated (Wilson et al, 2007). All the available data was critically analysed and revised equilibrium constants for the above reaction were obtained. The resultant line of best fit was:

$$\log K = -7640.3/T + 7.213$$

(T = absolute temperature- ºK). The use of these equilibrium constants agreed well with observed stibnite deposition at two geothermal fields.

REFERENCES

Dorrington, P. and Brown, K.L. (2000), Management of Stibnite Deposition at Ngawha, *NZ Geothermal Workshop Proceedings*, 163-167

Wilson, N, Webster-Brown, J., Brown, K.L. (2007) Controls on stibnite precipitation at two New Zealand geothermal power stations. *Geothermics*, **36**, 330 - 347