

THE ALKALINE SULFIDE HYDROMETALLURGICAL SEPARATION, RECOVERY AND FIXATION OF TIN, ARSENIC, ANTIMONY, MERCURY AND GOLD

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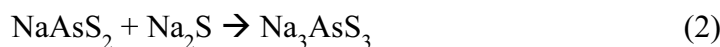
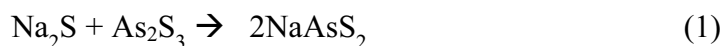
Abstract

Throughout the world, there are many orebodies or materials which have significant value but also contain arsenic, antimony, and mercury. As regulations on the transport, exposure, disposition and emission of these elements have become more stringent; it has become increasingly more difficult to derive the values from the resources. This paper outlines the fundamentals of alkaline sulfide hydrometallurgy and its successful application to arsenic, antimony and mercury bearing ores, concentrates, by-products, and other materials.

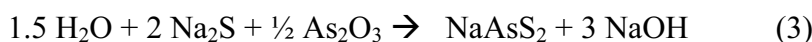
1. Fundamental Alkaline Sulfide Hydrometallurgy

Hydrometallurgical methods can be employed for treatment of gold, arsenic, antimony, tin and mercury containing materials, concentrates and ores as well as complex ones containing any number of metals. The alkaline sulfide system is one of these and is essentially a mixture of sodium sulfide and sodium hydroxide. This is a unique hydrometallurgical system as it is a very selective lixiviant for the distinct leaching of tin, gold, antimony, arsenic and mercury ^(1,2,3,4,5,6,7). Worldwide, it is employed industrially in the CIS, China and the United States for the production of antimony. ^(8,9,10,11,12,13,14,15)

As an example, when the system is applied to an arsenic containing material like orpiment, As_2S_3 , a solution of sodium thioarsenite is formed. This is illustrated as:



When applied to arsenic trioxide, As_2O_3 , sodium arsenite is also formed. The reaction is as follows:



Dissolution of elemental sulfur in sodium hydroxide is also used as a lixiviant for alkaline sulfide leaching of arsenic. The combination of sodium hydroxide and elemental sulfur results in the formation of species other than just sulfide (S^{2-}). Both

sodium polysulfide (Na_2S_x) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) are created along with sulfide. Figure 1 illustrates the equilibrium diagram for sulfur while Figure 2 illustrates the more commonly encountered meta-stable sulfur diagram.

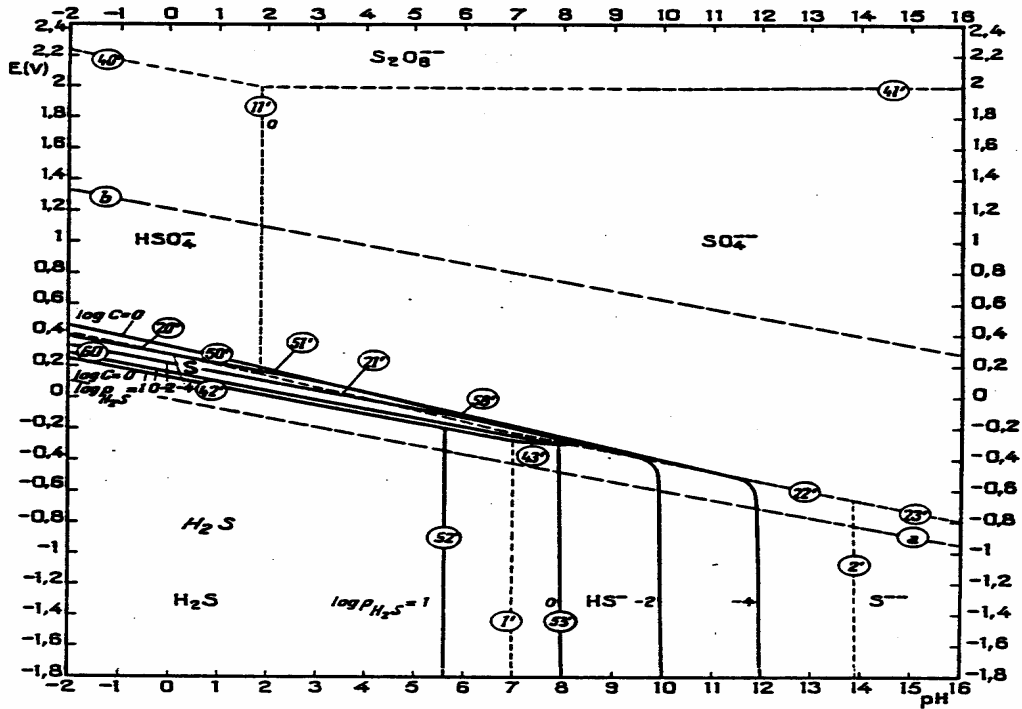


Figure 1. Equilibrium Eh-pH diagram for Sulfur

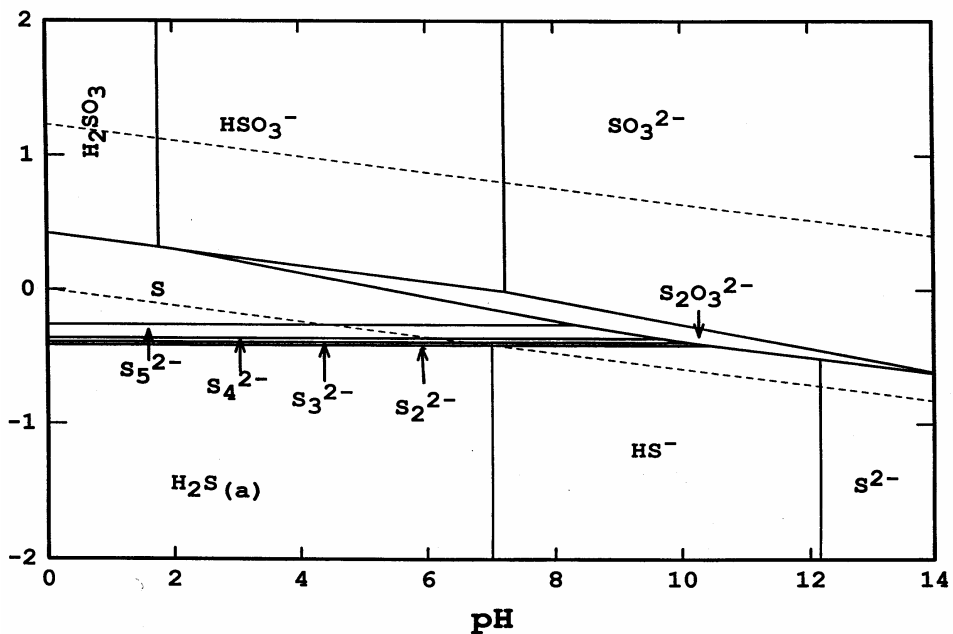
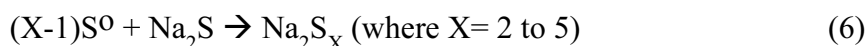
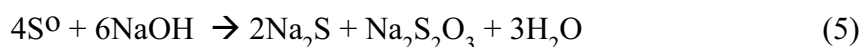
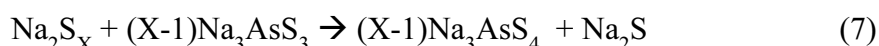


Figure 2. Meta-stable Eh-pH diagram for Sulfur

The generation of these predominant meta-stable species is illustrated simplistically in the following scenario.



Due to the oxidizing power of polysulfide on sodium thioarsenite, the major species in solution is normally sodium thioarsenate (Na_3AsS_4). This can be viewed as follows:



2. Applications of Alkaline Sulfide Hydrometallurgy to Arsenic and Antimony Leaching

The rest of this paper deals with the specific leaching application of the alkaline sulfide system to arsenic, antimony, and mercury bearing materials. The equations that describe the antimony and mercury dissolution are similar to the equations presented above for arsenic and therefore they won't be presented here. Also, due to space constraints, only the leach results for a series of lead smelter products will be shown in this paper. Several other applications of the alkaline sulphide leach treatment can be obtained by contacted one of the authors. The further treatment of the leach solutions is described elsewhere. The proven techniques and accompanying industrial flowsheets used to recover and stabilize arsenic with, for example, iron from the solutions is beyond the scope of this paper.

2.1 Alkaline Sulfide Hydrometallurgical Treatment of Lead Smelter Speiss

The formation of speiss in lead smelters is a common occurrence and poses process problems in that significant levels of precious metals are accumulated in the resultant arsenides and antimonides. An example of hydrometallurgical treatment follows.

Table I. Lead Smelter Speiss Head Sample Assay

<u>Cu,%</u>	<u>Ni,%</u>	<u>Sn,%</u>	<u>Cd,%</u>	<u>As,%</u>	<u>Sb,%</u>	<u>Pb,%</u>	<u>Fe,%</u>	<u>Zn,%</u>	<u>Au g/T,</u>	<u>Ag, g/T</u>
43.5	1.4	0.5	0.1	12.2	3.3	14.8	1.7	0.9	45.0	9000

Table II. Leach Testing Conditions

Leach Time = 6 Hr.
Percent Solids = 25%
Leach Temperature = 105 ^o C
Total Sulfur Concentration = 100 g/L
Free Hydroxide Concentration = 25 g/L

Table III. Leach Test Results

% of Metal Leached

Cu,%	Ni,%	Sn,%	Cd,%	As,%	Sb,%	Pb,%	Fe,%	Zn,%	Au,%	Ag,%
0.0	0.0	2.0	0.0	99.1	99.4	0.0	0.0	0.0	9.1	0.0

As seen, the alkaline sulfide leach was highly selective in removing only antimony, arsenic and some gold to solution.

2.2 Selective Recovery of Gold from Alkaline Sulfide Solutions

In the example cited above, it is essential in that any gold leached in the alkaline sulfide solutions be recovered. As shown in Figure 3, gold is soluble in the alkaline sulfide system. Gold lixiviation is the result of leaching by polysulfides and sulfides as shown in equation 8.

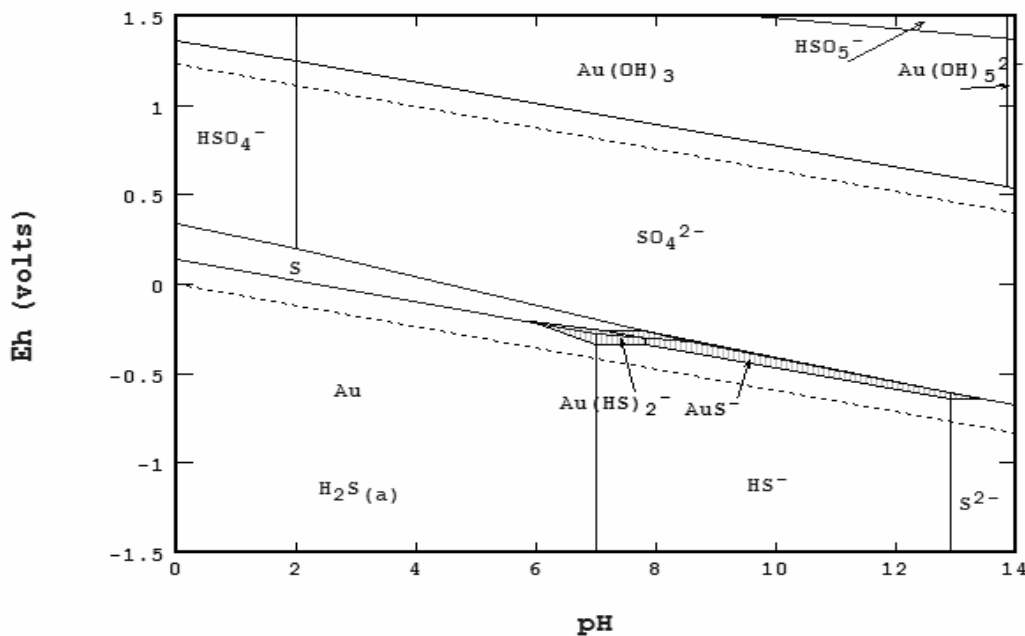
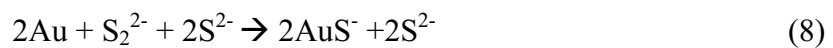


Figure 3. Equilibrium Species Eh-pH Diagram for Sulfur and Alkaline Sulfide Gold

Currently, studies are underway on the actual kinetics and mechanism of the alkaline sulfide system^(16,17,18).

Gold leached by the alkaline sulfide system is readily recoverable by several means including electrowinning, gaseous precipitation, chemical precipitation, cementation, solvent extraction and ion exchange. Conventional methods of gold recovery such as zinc or aluminum cementation are not applicable to this type of solution because of the dangers associated with stibine or arsine gas generation. As well, the conventional method of direct collection of gold by activated carbon does not work in these solutions as it does for gold cyanide solutions.

A proprietary gold recovery process has been adopted to quantitatively and selectively recover gold from complex alkaline sulfide solutions containing a mixture of metals such as arsenic, tin, mercury and antimony. This is illustrated by selectively removing gold from an alkaline sulfide leach solution containing these impurities. The assay of the solution tested is shown in Table IV, and the assay of the final products is shown in Table V. The overall results are presented in Table VI.

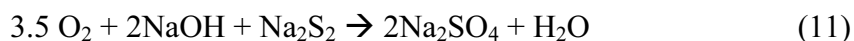
<u>Volume L</u>	<u>Au</u>	<u>Sb</u>	<u>As</u>	<u>Hg</u>	<u>Sn</u>
0.5	88.7 mg/L	21.0 g/L	5.31 g/L	274 mg/L	1.84 g/L

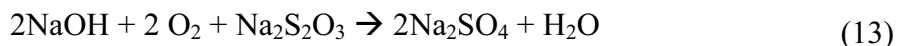
<u>Volume, L</u>	<u>Au</u>	<u>Sb</u>	<u>As</u>	<u>Hg</u>	<u>Sn</u>
0.5	14.4 ppm	21.1 g/L	5.21 g/L	274 ppm	1.89 g/L
Final Au Solid Sorbent Assay = 1561.4 g/T					

	<u>Liquid</u>	<u>Solid</u>
Gold	1.7%	98.3%
Antimony	100.0%	0.0%
Arsenic	100.0%	0.0%
Tin	100.0%	0.0%
Mercury	100.0%	0.0%

The proprietary substrate solids which have been employed to load the gold consist of several cheap and readily available materials and direct processing of the material is probably the cheapest and most effective method of refining the gold.

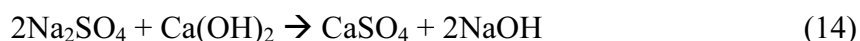
Also the waste alkaline sulfide solutions can be recycled for further gold leaching or further processed with low temperature oxidation to sodium sulfate, Na₂SO₄. This also oxidizes the arsenic to soluble sodium arsenate which can then be precipitated by conventional means using iron compounds. This oxidation process has been practiced in industry⁽¹⁹⁾. The resultant sodium sulfate, after arsenic removal, is further treated by purification and crystallization to produce high grade, marketable sodium sulfate. This process is illustrated simplistically in the following scenario.



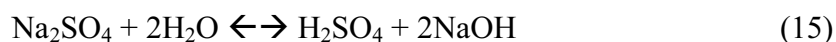


This versatile and environmentally benign chemical may then be sold to and utilized in industries such as pulp and paper, glass, ceramics, detergents, textile dyes, mineral feed supplements, bleach and photography. As such, there are minimal environmental or toxicological issues in the use of alkaline sulfide gold recovery as the waste products become value added, marketable by-products.

As well the sodium sulfate produced can be used to regenerate the sodium hydroxide needed in the process in a manner analogous to industrial dual alkali scrubbing systems⁽²⁰⁾. This is as follows:



The clean gypsum product can then be marketed and used in such applications as agricultural soil amendments or as an additive in primary cement manufacture. In addition, initial efforts are underway and have been successful in regenerating the necessary H₂SO₄ and NaOH reagents from the Na₂SO₄ by-product. The details of this process will be given in future publications and may be illustrated as follows:



2.3 Alkaline Sulfide Hydrometallurgical Treatment of Lead Smelter Copper Dross Flue Dust

The formation of arsenic and antimony laden dusts in the processing of lead is commonly encountered. An example of hydrometallurgical treatment of this arsenic trioxide bearing materials follows:

Table VII. Copper Dross Flue Dust Head Sample Assay

In, %	Pb,%	Sb,%	As,%	Zn,%
0.3	46.0	9.0	12.0	11.0

Table VIII. Leach Testing Conditions.

Leach Time = 6 Hr.
 Percent Solids = 25%
 Leach Temperature = 105^o C
 Sulfide Concentration = 100 g/L
 Free Hydroxide Concentration = 10 g/L

Table IX. Leach Test Results

% of Metal Leached				
In, %	Pb,%	Sb,%	As,%	Zn,%
0.0	0.0	95.0	99.0	0.0

2.4. Alkaline Sulfide Hydrometallurgical Treatment of Lead Softening Skims

The formation of arsenic and antimony skims in lead refining is commonly encountered. An example of the application of the alkaline sulfide hydrometallurgical treatment follows.

Table X. Lead Softening Skims Head Sample Assay

<u>Pb,%</u>	<u>Sb,%</u>	<u>As,%</u>
52.9	31.7	3.3

Table XI. Leach Testing Conditions.

Leach Time = 6 Hr.
Percent Solids = 25%
Leach Temperature = 105^o C
Sulfide Concentration = 100 g/L
Free Hydroxide Concentration = 10 g/L

Table XII. Leach Test Results

% of Metal Leached

<u>Pb,%</u>	<u>Sb,%</u>	<u>As,%</u>
0.0	89.0	96.0

2.5 Alkaline Sulfide Hydrometallurgical Treatment of Copper Enargite Concentrates

In many parts of the world, enargite, Cu₃AsS₄, occurs as a primary copper mineral. Alkaline sulfide hydrometallurgy can be effective in treating these types of ores and concentrates. This is illustrated as follows:

Table XIII. Copper Enargite Concentrate Head Sample Assay

<u>Cu, %</u>	<u>As, %</u>	<u>Sb, %</u>	<u>Au, g/T</u>
30.1	10.7	1.2	35.1

Table XIV. Leach Testing Conditions

Leach Time = 1 Hr.
Percent Solids = 25%
Leach Temperature = 105^o C
Sulfide Concentration = 100 g/L
Free Hydroxide Concentration = 10 g/L

Table XV. Leach Test Results.

% of Metal Leached			
<u>Cu, %</u>	<u>As, %</u>	<u>Sb, %</u>	<u>Au, %</u>
0.0	99.2	99.7	14.3

In this case, a high grade, 38% copper concentrate with minimal arsenic was produced for treatment by smelting. The gold in solution was recovered with the technology portrayed earlier in the paper and the arsenic was precipitated and stabilized with iron after oxidation of the alkaline waste solutions.

3. Applications of Alkaline Sulfide Hydrometallurgy to Antimony and Mercury Leaching

As a further example of the flexibility of the alkaline sulfide leaching technology the following summary of the Center for Advanced Mineral and Metallurgical Processing (CAMP) is presented below.

The Roznava district in Slovakia has long been known for its copper, silver and antimony bearing tetrahedrite ores.. Mercury is also found in conjunction with this ore complicating the processing. A typical flotation concentrate of this type is shown in Table XVI. In the past, pyrometallurgical roasting has been utilized to remove antimony, arsenic and mercury from the concentrates and ores. This has resulted in long term existing environmental impacts in the region.

Table XVI. Roznava Tetrahedrite Concentrate.

<u>Sb, %</u>	<u>As, %</u>	<u>Hg, %</u>	<u>Cu, %</u>	<u>Fe, %</u>	<u>Ag, ppm</u>	<u>Au, ppm</u>	<u>TS, %</u>
17.3	1.85	0.55	26.1	12.4	6,400	2.0	22.0

Utilizing alkaline sulfide hydrometallurgy, as practiced industrially, extensive studies were undertaken in the United States to produce and treat Roznava concentrates. The primary issues of interest to be addressed in this paper were solubilization of antimony and mercury, purification of the leach liquors, the deportment of the mercury and the recovery of gold from solution.

The leaching of the concentrate was straightforward. The conditions utilized are shown in Table XVII. These conditions and results are reflective of closed cycle testing of the system that includes extensive recycling of solutions depleted after antimony recovery. This more accurately reflects plant conditions.

Table XVII. Alkaline Sulfide Leach Testing Conditions.

Leach Time = 12 Hr.
 Roznava Concentrate = 100 g/L
 Leach Temperature = 105^o C

Sulfur Addition = 20 g/L
 Sodium Hydroxide = 35 g/L
 Sb Leached = 95.0 % As Leached = 60.0 %
 Hg Leached = 95.0 % Au Leached = 20.0 %
 Cu Leached = 0.0 % Ag Leached = 0.0 %

The mercury in solution must be separated for successful antimony electrowinning recovery. This can be done in several ways. Selective cementation of mercury from solution is one methodology and it can be accomplished by several means utilizing copper, antimony, iron and sulfur. This may be illustrated as;



For the actual proposed plant an alternative patented technology was actually chosen for solution purification. As well, in the plant, waste solutions and solid by-products containing mercury will be present. For example mercury will be precipitated in conjunction with by-product sodium hydroxyantimonate production by pressure oxidation as follows;



The mercury bearing solid sodium hydroxyantimonate is then relieved of its mercury content via selective lixiviation. The mercury is then recovered as a waste product, stabilized and stored while the cleaned sodium antimonate is either recycled into the plant or marketed.

The gold leached by the alkaline sulfide system is readily recoverable by several means including electrowinning, gaseous precipitation, chemical precipitation, cementation, solvent extraction and ion exchange. Further, a novel gold recovery method has been adopted to quantitatively and selectively recover leached gold from complex alkaline sulfide solutions. This is illustrated by selectively removing gold from an alkaline sulfide leach solution containing impurities. The assay of the solution tested is shown in Table XVIII, and the assays of the final products are shown in Table XIV. The overall results are presented in Table XV.

<u>Table XVIII. Alkaline Sulfide Gold Solution Assay.</u>					
<u>Volume L</u>	<u>Au</u>	<u>Sb</u>	<u>As</u>	<u>Hg</u>	<u>Sn</u>
0.5	88.7 ppm	21.0 g/L	5.31 g/L	274 ppm	1.84 g/L

Table XIV. Alkaline Sulfide Gold Solution Final Assay.

<u>Volume, L</u>	<u>Au</u>	<u>Sb</u>	<u>As</u>	<u>Hg</u>	<u>Sn</u>
0.5	1.5 ppm	21.1 g/L	5.21 g/L	274 ppm	1.89 g/L
Final Au Solid Sorbent Assay = 1561.4 g/T					

Table XV. Overall Gold Selectivity and Recovery.

	<u>Liquid</u>	<u>Solid</u>
Gold	1.7%	98.3%
Antimony	100.0%	0.0%
Arsenic	100.0%	0.0%
Tin	100.0%	0.0%
Mercury	100.0%	0.0%

4. Summary

From the cited examples in the paper, which utilized fundamental principles of alkaline sulfide hydrometallurgy as well as its industrially proven applications for the selective arsenic, antimony, and mercury removal, it is obvious that ores, concentrates and materials containing these can be effectively treated while also achieving selective gold recovery where required.

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