

Gold Mines Water Arsenic Elimination by Precipitation with Iron Sulphates

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Abstract: Arsenic is one of the most toxic metals derived from the natural environment. Potentially toxic arsenic compounds are found in every aspect of our environment. Inorganic arsenic occurs on earth naturally in small amounts. Humans may be exposed to arsenic through food, water, and air. The major cause of human arsenic toxicity is from contamination of drinking water from natural geological sources rather than from mining, smelting, or agricultural sources (pesticides or fertilisers). Arsenic toxicity is a global health problem affecting many millions of people. Contamination is caused by arsenic from natural geological sources leaching into aquifers, contaminating drinking water and may also occur from mining and other industrial processes.

The objective of this study is to drop down the concentration of As in solution to 0.1 mg/L in accordance with Malian and international standards and with optimum cost.

The article is about the reduction of arsenic (As) concentration in the aqueous phase of mine tailings resulting from the leaching of sulphide ores in laboratory conditions. Analysis of the solution after leaching (leachate) provides information on the transfer of arsenic in the aqueous phase. For this work we used 10 samples from different sampling areas. The experimental protocol was developed to study the precipitation of As by Fe (II and III) sulphates. The results provide information on the efficiency of the titration and the necessary volume of the titrant solutions to obtain the As concentration in accordance with Malian and international standards, which is 0.1 mg/L. The obtained results were satisfactory, that related to the arsenic concentrations were reduced to 0.095 ppm using 9 mL of iron (II) sulphate solution and to 0.091 ppm using only 7 mL of iron (III) sulphate solution. In term of cost comparison, iron (III) solution cost less by 62% than iron (II) solution and on quantitative base comparison iron (III) sulphate was consumed less by 74% than iron (II) sulphate.

Keywords: Arsenic, Leach, Sulphide, Tail solution

1. INTRODUCTION

Third gold producer in Africa, mining is a strategic industrial area in Mali. The multiplication

of exploration activities has resulted in several sulphide deposits emerging. During the exploitation of these deposits, mining waste can pose significant environmental problems because of the high reactivity of sulphide minerals (such as pyrite and pyrrhotite). [1,3,4]

Arsenic (As) is a recurrent metalloid in many sulphide deposits, such as certain copper-bearing porphyries, epithermal gold deposits or volcanogenic massive sulphide deposits [2,3], among which are found in Mali the deposits of the mines of the Loulo Goukoto complex in the Kayes region, Syama in the Sikasso region. In the liquid phase of the tailings of some mine deposits, there are essentially two forms of arsenic: arsenic (III) is common, and arsenic (V) is rare. [19,20,21]

The toxicity of arsenic is well known, an effective control of the quantities of arsenic released in the mining residues must therefore be put in place, to avoid significant contamination of the underground water tables located nearby. Thus, in recent years, stricter legislation at the international level in terms

of mining operations has led to the lowering of tolerance thresholds for the concentrations of heavy metals and metalloids in mining effluents. (WHO. 2000). The tolerance threshold is 0.1 mg/L. [5]

In this article, arsenic in the aqueous phase of the leaching residues from the laboratory test is precipitated by iron (II) and iron (III) sulphates to have an arsenic concentration below the tolerance threshold. Thus, it will be determined among the two reagents which is economically profitable.

2. MATERIAL AND METHODS

Study is lead in Syama mining. Located in the south of Mali, West Africa, the mine is approximately 30kms from Ivory Coast border and 300km southeast of the capital Bamako. Syama benefits from two fully operational parallel sulphide and oxide processing plants with site production capable of more than 250,000oz/pa. Ore for sulphide circuit is currently sourced from the Syama Underground stockpiles while satellite pit supplies oxide ore to the oxide circuit. [6]



Figure1. Carte of Africa with Syama gold mine location in Mali [6]

Information about the sample: The samples have been taken from one of Syama pit, the pit was oxide Open Pit and it’s planned to start the underground phase by extracting the sulphide ore. The difficulty with this underground ore is that the gold is double refractory. The first level of refraction is driven by gold encapsulated in the pyrite (FeS₂) and arsenopyrite (FeAsS). The second level of refraction is driven by the presence of organic carbon, whose concentration can reach 1% in the feed of the treatment circuit. The metallurgical laboratory test propose is to determine the residual arsenic in the tail’s solutions after ore communitation and valorisation. The raison is due to tails solution is planned to be reclaimed and used in the processing plant. This practice is to maximize water recirculating rate into the plant.

In the table 1, is listed the name of samples and the drilling holes depth where the samples are coming from.

Table1. Samples ID and depth from which they were taken

Number	Sample ID	Hole ID	Depth From, m	Depth To, m	Weight, Kg
1	SY522544	TARC865	21	22	5.3
2	SY522548	TARC865	25	26	6.4
3	SY522563	TARC903	55	56	4.5
4	SY525568	TARC903	60	61	4.9
5	SY522572	TARC865	69	70	5.1
6	SY522578	TARC865	75	76	6.7
7	SY522583	TARC865	80	81	6.1
8	SY522593	TARC865	90	91	4.3
9	SY522603	TARC865	100	101	5.2
10	SY522613	TARC865	110	111	5.2

Sample treatment: Samples have been dried in the oven at 105 ± 10 degrees, for moisture elimination. The weight of each sample was determined and registered in above table (Table 1). Leaching process has been performed on each sample by using standard BRT (Bottle Rolling Test) to reproduce the treatment condition in the plant (Figure 2). Obtained slurry was filtered, all tails solutions were uniformly mixed to get one homogeny solution and composite of the tail solution has been submitted to laboratory for analysis.

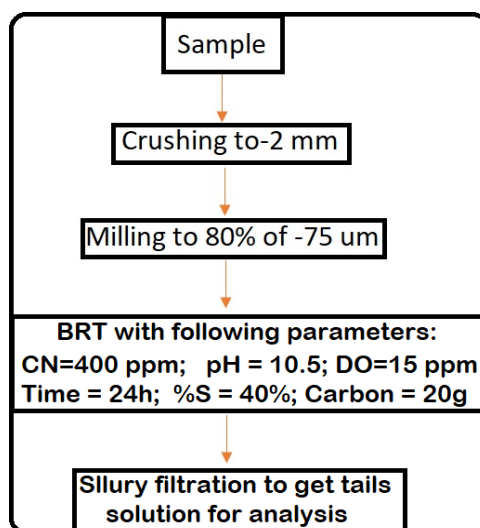


Figure2. Parameters of BRT test processed to obtain the tail solution

Arsenic occurs in the environment in four oxidation states (As^{+3} , As^{+5} , As^0 and As^{-3}) in inorganic as well as in organic forms. [7,8,9] Inorganic arsenic comprises the two oxyanions arsenite As (III) and arsenate As (V).

Preparation of solution for titration:

20 mg of iron (II) sulphate was weighed on an electronic balance and diluted in a 100 mL volumetric flask (due to 80% water and 20% solid) to obtain the titration solution in iron (II). The solution from the BRT was dosed with the iron (II) solution. The initial volume of dosage was 5 mL, the volume was gradually increased by 2 mL for each subsequent sample. A total of 10 samples, with a volume of 500 mL each.

For iron (III) solution preparation, the same process as the preparation of iron (II) solution was used except that 5ml of hydrogen peroxide was add into the solution.

Methods of analysis

ICP -OES (Inductive Coupled Plasma Optical Emission Spectrometry) to determine the metals in tail solution.

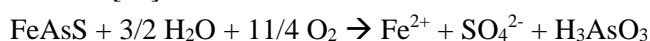
The request was to identify the metal in solution by ICP -OES (Inductive Coupled Plasma Optical Emission Spectrometry). ICP is the most applied detection technique, application of it has great capabilities since it can be used as a highly sensitive and element specific detector. The method consists of ionizing the sample by injecting it into an argon plasma. The sample, under finely divided form, is introduced into the plasma and undergoes vaporization and ionization state changes. The electrons of the excited (ionized) atoms when they return to the ground state emit a photon whose energy emitted is characteristic of the element. The light emitted by the element sought is then detected and measured. Its intensity is compared to that emitted by the same element contained in a sample of known concentration. [10,11]

- Mercury have been analysis by FIMS (Flow Injection Mercury Systems).
- pH has been analysis by SPLP (Synthetic Precipitation Leaching Procedure).
- Arsenic Analysis Kit - Lovibond water was used to determine arsenic concentration after titration with iron (II) sulphate solution.

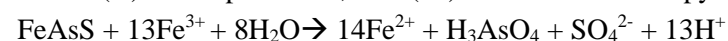
3. RESULTS AND DISCUSSION

The oxidation-reduction couples of iron sulphate

The As contained in the sulphides can be liberated by oxidation in the mine waste medium. Arsenopyrite, one of the most common arsenic sulphides, oxidizes as follows according to the reaction [12]:



Arsenic is released in solution in trivalent form, but depending on the redox potential, it can oxidize to arsenic (V). If the pH is low, iron (III) can oxidize arsenopyrite as in the case of pyrite [13]:

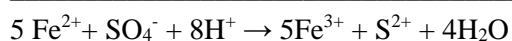
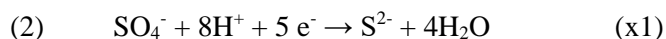


It is, however, arseniferous pyrite which releases the most arsenic in mine wastewater from the processing of sulphide ores. Indeed, pyrite is generally the most abundant sulphide in sulphide mining waste. Substitution of a sulfur atom by an arsenic atom in the crystal lattice of pyrite creates p-type semiconductor regions that trap electrons [14,15]. The electrical and ionic conductivity of pyrite is thereby improved, and its oxidation kinetics accelerated. In addition, under oxidizing conditions, sulfur vacancies can form in the crystal lattice of pyrite which increases its alterability [16].

The oxidation-reduction equation that takes place in the solution containing iron ions and SO₄ sulphate ions, in an acid medium:

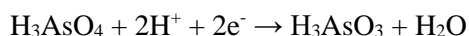
Fe²⁺ / Fe³⁺ : couple reducer 1

SO₄⁻ / S²⁺ : couple oxidizer 2

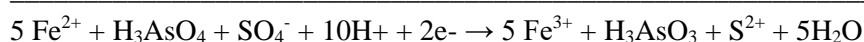
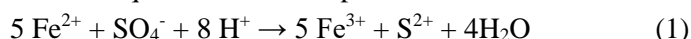


Oxidation of As (III) to As(V)

The As (III) to As (V) redox system can be written as follows:



Balance equation of iron sulphate on Arsenic:



H₃AsO₄ (Arsenic V); H₃AsO₃ (Arsenic III).

The results of submitted to laboratory tail solution composite is indicated in the table 2. The value of arsenic indicated in the table 2 is total arsenic, which mean all inorganic and organic arsenic found in aqueous solution (the sum of As⁺³, As⁺⁵, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) [17,18]).

Table2. Metals in composite tail solution

Compound	LOR	Unit	Result
EG020C: Leachable Metals by ICP-OES			
Aluminium	0.1	mg/L	0.2
Arsenic	0.01	mg/L	5.87
Barium	0.1	mg/L	<0.1
Bismuth	0	mg/L	<0.001
Cadmium	0	mg/L	<0.001
Cobalt	0.01	mg/L	0.03
Chromium	0.01	mg/L	<0.01
Copper	0.01	mg/L	1.93
Lithium	0	mg/L	0.018
Manganese	0.01	mg/L	0.01
Molybdenum	0.01	mg/L	0.04
Nickel	0.01	mg/L	0.02
Lead	0.01	mg/L	<0.01
Thallium	0.01	mg/L	<0.01
Vanadium	0.01	mg/L	<0.01
Zinc	0.1	mg/L	<0.1
Iron	0.05	mg/L	4.520
Silver	0.01	mg/L	<0.01
Strontium	0.01	mg/L	1.410
Titanium	0.01	mg/L	0.010
Yttrium	0	mg/L	<0.001
Zirconium	0.01	mg/L	<0.005
EG035C: Leachable Mercury by FIMS			
Mercury	0	mg/L	<0.001

LOR - Limit Of Reporting

Table3. Rate of arsenic precipitation by Fe (II/III) sulphate

Sample	Titration by Fe(II)			Titration by Fe(III)			Malian and international standard, mg/L
	Dose of Fe(II), mL	As concentration after titration, mg/L	Precipitation rate, %	Dose of Fe(III), mL	As concentration after titration, mg/L	Precipitation rate, %	
1	1	3.235	44.89	1	3.01	48.72	0.1
2	2	2.105	64.14	2	1.995	66.01	0.1
3	3	1.64	72.06	3	1.05	82.11	0.1
4	4	0.805	86.29	4	0.735	87.48	0.1
5	5	0.51	91.31	5	0.31	94.72	0.1
6	6	0.405	93.10	6	0.192	96.73	0.1
7	7	0.265	95.49	7	0.091	98.45	0.1
8	8	0.11	98.13	8	0.045	99.23	0.1
9	9	0.095	98.38	9	0.001	99.98	0.1
10	10	0.04	99.32	10	0	100.00	0.1

According to the result, the concentration of arsenic in the composite tail solution is 5,87 mg/L which is higher than the tolerance threshold (0,1 mg/L). It's mean that the slurry can't be send to the tails storage facility (TSF) and contained solution reclaimed to the process plant without dropping down the level of contained arsenic.

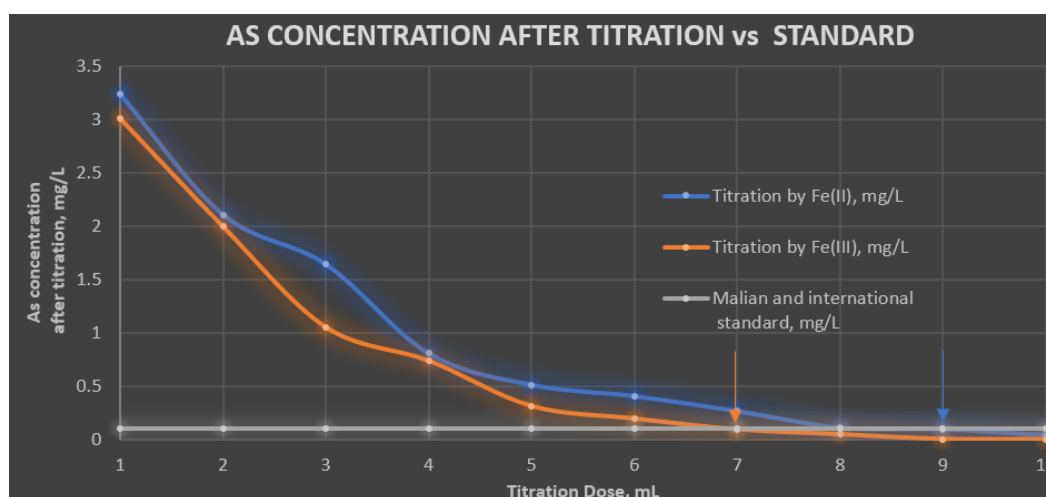


Figure3. Solution residual As after titration by Fe(II) and Fe(III)

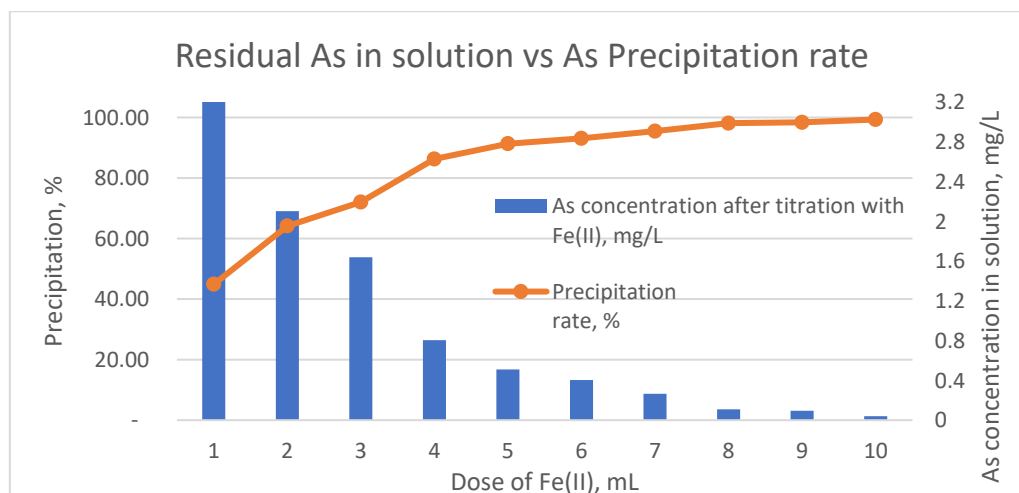


Figure4. As precipitation rate titrated by Fe(II)

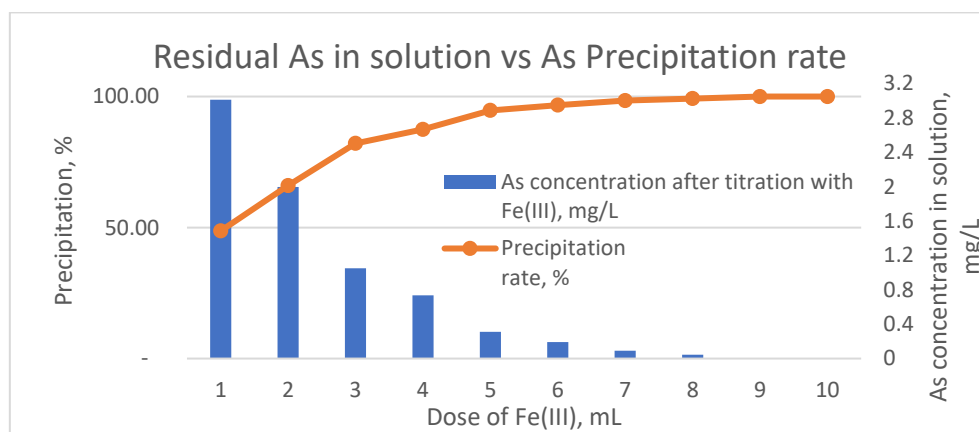


Figure 5. As precipitation rate titrated by Fe(III)

To overcome the issue with arsenic concentration in the solution, series of titrations have been performed using iron (II and III) sulphate solutions. The results of titration are indicated in the table 3 (Figure 3,4&5). Lj. V. Rajaković and Others in 2013 in Serbia and Kante M. in 2022 in Mali got the similar results when performed titration of As in solution. The concentrations were respectively 0.0998 mg/L and 0.0992 mg/L. [2,19]

For the sake of comparison, the complete data have been reconciled in Table 3. Thus with an initial concentration of 5,87 mg/L of arsenic in the leachate [Table 2], the results show us that with a volume of the titrant solution of 9 mL of iron (II) sulphate, a precipitation of 98.3% of arsenic is observed, i.e. an arsenic concentration of 0.095 mg/L on the one hand; and on the other hand with a volume of 7 mL of the titrant solution of iron (III) sulphate, a leachate containing 0.091 mg/L of arsenic is obtained, i.e. a precipitation of 98,45% . This indicates that the iron (III) sulfate solution is more precipitating than the iron (II) sulfate solution in the arsenic titration. In addition, the volume of the iron (III) sulphate solution used thereby is 28.57% less than that of the iron (II) sulphate.

A comparative study for consumption of iron (II) and iron (III) solution have done in table 4. According to results:

In term of consumption, iron (III) sulphate was consumed less by 74% (weight) than iron (II) sulphate;

In term of cost, iron (III) solution cost less by 62% than iron (II) solution.

Table 4. Cost and consumption comparisons

Reagent	Consumption		Cost	Expected after titration As	Eq solution volume treated
	L	Kg			
Unit			\$	ppm	m ³
Fe(II)	18	3.60	4.14	0.095	1
Fe(III)	14	2.07	2.39	0.091	1
Peroxide	0.7	-	0.16		

4. CONCLUSION

The control by analysis of arsenic, in the mining industry with arsenic in the feed ore, is one of high importance for human health related to its toxicity. However, a point common to the entire mining industry lies in the production of large quantities of mining waste, resulting from the processing of ores (solid and liquid) during exploitation. Arsenic is more of a problem for the mines because it is not often recovered and gives the tailings that contain it increased toxicity.

It is to overcome this problem that the present work proposes a solution by the titration, on a laboratory scale, of the composite of the leaching solution of a concentration of 5.78 ppm in arsenic by solutions of iron (II) and iron (III) sulphates. The obtained results were satisfactory, that related to the arsenic concentrations were reduced to 0.095 ppm using 9 mL of iron (II) sulphate solution and to 0,091 ppm using only 7 mL of iron (III) sulphate solution. In both cases arsenic contained in the solution after titration is lower than indicated Malian and international norms (0.1 ppm). In term of

cost comparison, iron (III) solution cost less by 62% than iron (II) solution and on quantitative base comparison iron (III) sulphate was consumed less by 74% than iron (II) sulphate. The recommendation will be to put in place for the ore valorisation a unite with following dosing set points: 14 L of iron (III) sulphate solution mixed with 0,7 L of peroxide [Table 4] for each 1m³ of leach solution. The expected arsenic precipitation in solution is estimated as 98,45%.

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