

ARSENIC MOBILIZATION FROM SULFIDIC MATERIALS FROM GOLD MINES IN MINAS GERAIS STATE

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Acid drainage results from exposition of sulfides to the atmosphere. Arsenopyrite is a sulfide that releases arsenic (As) to the environment when oxidized. This work evaluated the As mobility in six sulfidic geomaterials from gold mining areas in Minas Gerais State, Brazil. Grained samples (<2 mm) were periodically leached with distilled water, during 70 days. Results suggested As sorption onto (hydr)oxides formed by oxidation of arsenopyrite. Low pH accelerated the acid generation, dissolving Fe oxihydroxides and releasing As. Presence of carbonates decreased oxidation rates and As release. On the other hand, lime added to a partially oxidized sample increased As mobilization.

Keywords: arsenopyrite; acid mine drainage; contamination.

INTRODUCTION

Acid mine drainage (AMD) results from a set of chemical, electrochemical and microbiological reactions, risen from exposure of sulfide bearing geological materials to the atmospheric oxygen and water.¹ Under such conditions there is a net generation of sulfuric acid, decreasing pH of the drainage water and increasing solubility and leaching of toxic elements as heavy metals and metalloids.²⁻⁴ Consequently, there are increasing risks for toxic metals and metalloids incorporation in biological systems and so, bioaccumulation and biomagnification processes in the trophic chain.

Arsenopyrite is a sulfide (AsFeS) commonly found in gold mine areas.^{5,6} Its oxidation produces arsenic and sulfur oxiacids (e.g. H_3AsO_3 , H_3AsO_4 , H_2SO_4). Arsenic is toxic at low concentrations and sulfuric acid is responsible by the pH drop.⁷ The rate of sulfides oxidation depends on several factors, including the amounts of arsenopyrite (e.g. AsFeS), grain size distribution, temperature and the exposure time of the material to the atmospheric water and oxygen. Catalytic action of the *Acidithiobacillus* aggravates the problem under acid medium, at $pH < 3$, which stimulates bacterial activity.⁸

Ingestion of water is considered the main source for As contamination. The most noticeable reports are mass contamination cases that took place in Bangladesh,^{9,10} Taiwan^{11,12} and Chile.¹³ In Brazil, the Iron Quadrangle is one of the affected regions in Minas Gerais State. Most impacted areas are close to gold mines, as in Nova Lima, Raposos, Mariana and Santa Bárbara districts.¹⁴⁻¹⁶

Several researchers showed that As adsorption onto iron oxides decreases as the pH increases.¹⁶⁻²⁰ On the other hand there are reports of increasing As (III) sorption as the pH increases from 3 to

the neutral, when the adsorbent is a sulfide as troilite (FeS) or pyrite (FeS₂).²¹ Release of As from arsenopyrite structure, by oxidation, also decreases at increasing pH, mainly due to the drop of bacterial activity.^{8,9}

Face to the need for controlling As dispersion in the environment, this research was performed in order to study the mobility of As in samples of sulfidic materials from gold mine areas in different geological scenarios at Minas Gerais State, Brazil. Mobility of As was evaluated by simulating AMD in leaching columns containing naturally acidic and alkaline samples.

EXPERIMENTAL

Samples collection

Samples of six sulfidic materials (Table 1) were collected from gold mine areas in Riacho dos Machados, Santa Bárbara and Paracatu districts in the Minas Gerais State, Brazil (Figure 1). Samples were stored in plastic bags, identified and prepared for analytical characterization.

Table 1. Samples procedure and identification

Identifi- cation	Type of sample	Procedure	Observation
19 PT	Overburden	Paracatu	Old topsoil
34 PT	Ore	Paracatu	B2 ore partially oxidized
61 SB	Overburden	Santa Bárbara	Probe sample
62 SB	Ore	Santa Bárbara	
92 RM	Overburden	Riacho dos Machados	Partially oxidized
93 RM	Ore	Riacho dos Machados	Partially oxidized

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Figure 1. Minas Gerais State map, showing the districts where samples were collected

Chemical analyses

Samples were characterized by potentiometric determination of pH in a 1:2.5 (sample:water) aqueous suspension²² and total contents of As, S and Fe. Potential acidity (PA) and neutralizing potential (NP) were also determined. The acid-base accounting (ABA) was calculated by the difference between PA and NP, in mols of acidity per ton of material. Grained samples (< 2 mm) were used to the pH determination. Other analyses were performed in < 100 mesh ground samples.

Potential acidity (PA) determination

The method for PA determination was proposed by O'shay *et al.* (1990) with modifications by Corrêa *et al.*²³ 100 mL of 30% H₂O₂ were gently added to 2.0 g of ground samples and boiled for 60 min in 250 mL erlenmeyers flasks with reflux condenser. This procedure was repeated with 50 mL of peroxide solution and then suspensions were cooled at room temperature. 1.0 mL of 0,0157 mol L⁻¹ CuCl₂·2H₂O solution was added and suspensions were boiled for 15 min to decompose the excess of peroxide. Solutions were filtered under vacuum after cooled at room temperature and transferred to 200 mL volumetric flasks made volume with 1.0 mol L⁻¹ CaCl₂. Aliquots (50 mL) were boiled to eliminate dissolved CO₂ and acidity was determined by titration with CO₂ free 0.01 mol L⁻¹ NaOH solution.

Neutralization potential (NP) determination

NP of the samples was evaluated by the technique reported by EMBRAPA.²² 50 mL of 0,5 mol L⁻¹ HCl solution were added to 5,0 g of sample in 250 mL erlenmeyers flasks. Suspensions were boiled for 5 min and then cooled at room temperature. After filtered, solutions were boiled again to eliminate dissolved CO₂, cooled and the HCl excess was titrated with CO₂ free 0.5 mol L⁻¹ NaOH solution.

Total arsenic and sulfur contents

Samples (1.0 g) were digested with 50 mL of *aqua regia* (1:3 HNO₃:HCl) solution in flasks with reflux condenser by boiling suspensions for 30 min in a hot plate, as reported by Soares *et al.*²⁴ After cooling at room temperature, the extracts were suspended with 50 mL of distilled water and solutions were filtered to 250 mL volumetric flasks made volume with deionized water. Then, contents of As and S in the extracts were determined by ICP-OES.

Leaching tests

Samples were submitted to simulated weathering tests in order to evaluate the sulfide oxidation rate and As solubilization. 150 g of previously grained samples (< 2 mm) were dried at 65 °C for 24 h and mixed to 150 g of inert sand (ground and washed quartz) in leaching columns. Previous tests indicated the need of ground quartz in order to set an adequate porosity to allow a suitable flux of leachates.

The experiment was performed in a completely randomized design with seven treatments (6 sulfidic materials + 1 blank) in three replications. Columns were leached with 250 mL of deionized water (corresponding to an 88.5 mm water column) every 2 weeks, during 70 days. Weight and pH of the leachates were determined and 20 mL aliquots were acidified with 5 mL of HCl 1 mol L⁻¹ just after collection in order to avoid precipitation reactions. Contents of As, Fe and S were then determined by ICP-OES.

Analyses of variance and Pearson correlation coefficients were performed with the software Statistics and Genetics Analyses System 8.1 (SAEG).²⁵

RESULTS AND DISCUSSION

Acid-base accounting (ABA) and pH of the samples

Alkaline samples from Santa Bárbara (pH>7.0) showed negative ABA values (Table 2). Conversely, ABA values were positive in acidic samples from Riacho dos Machados (pH<4.0). This suggest that pH in aqueous suspension (1:2.5) can indicate, in some extent, the acid-forming materials, probably due to the previous oxidation of the samples. Nevertheless, results pointed out samples from Paracatu as acid-forming materials (positive ABA) in spite of relatively high aqueous pH, mainly in sample 19 which is close to neutral. This sample is a partially oxidized overburden that has been limed to be used as topsoil. Probably oxidation of sulfides promoted partial dissolution of lime during storage, but the remaining sulfides are high enough to explain the current positive ABA value.

According to the mineralogy reported by Fonseca,²⁶ carbonates occur just as accessory minerals, besides sulfides like pyrrhotite and arsenopyrite in Riacho dos Machados formation. This means that contents of carbonates are low and in agreement with NP lower than PA values to the RM samples. On the other hand, ABA data to the samples from Santa Barbara agreed well with mineralogical characterization performed by Mello *et al.*²⁷ These authors found pyrrhotite, arsenopyrite and substantial amounts of carbonates in samples from this region.

Predictive technology of acid drainage quality can be performed by static and dynamic tests. The main problem of static tests is that they don't consider the kinetics of reactions. Because of the variations in kinetics between acid and alkaline production, balancing the acid account against the base account, without taking into consideration long-term weathering, can lead to erroneous predictions.²⁸ Therefore, estimates are not confident for samples with low ABA values (close to zero). According to Mello *et al.*²⁹ sulfides can generate acid drainage even in the presence of carbonates in samples with negative ABA values. This implies that oxidation reactions are faster than carbonates dissolution. On the other hand, drainage can be alkaline or close to neutral in samples presenting positive ABA values when stable sulfides produce slow oxidation. In these types of samples ABA values are not suitable to prediction of acid drainage and dynamics tests of simulated weathering, like leaching columns, are warranted.

Total As and S contents of the samples

Contents of arsenic and sulfur were higher in ore samples than in overburden ones. Anyway, the contents can be considered very high in all samples (Table 3). Lower values of the As/S ratio were obtained to samples from Riacho dos Machados (92 and 93), which also presented lower pH values (Table 2). Conversely, the higher As/S ratio was found in the ore sample from Santa Bárbara, which was alkaline. These results are probably related to the previous weathering of the samples. At low pH the oxidation rate is increased due to the microbiological catalysis by *Acidithiobacillus ferrooxidans* bacteria.⁸ Consequently the arsenic is released to the medium decreasing its content in the remaining sample. On the other hand the oxidation rate is lower at high pH and the iron (hydr)oxides precipitate retaining arsenic in the sample. It is very well known that Fe-(hydr)oxides can be formed as products of sulfide oxidation and retain As at pH higher than 3.5.^{16,18-20} Under lower pH, such (hydr)oxides are unstable and the iron is leached far away from the samples together with sulfates and arsenic.

Leaching tests

Cumulative amounts of As leached from columns were high to the acidic samples from Riacho dos Machados, but very low to the alkaline samples from Santa Bárbara. Samples from Paracatu formation leached low amounts of arsenic (Figure 2). In general, the higher the pH the lower was the leached As, except to the samples from Paracatu, where sample 19 presented higher pH and higher amounts of leached arsenic in relation to sample 34. The As/S relation in sample 19 (0.27) is slightly higher than in sample 34 (0.22) but does not explain higher As leaching from sample 19. Lime has been added to sample 19, differently of naturally occurring carbonates from Santa Barbara samples. These results suggest that behavior of As under high pH is different depending on the lime source. Probably previous oxidation retained arsenic adsorbed onto iron oxides in sample 19. Under such conditions lime addition promoted As desorption and consequently higher amounts of As

were leached from this sample than from sample 34.

In general the amounts of As leached from columns were low to the samples with pH higher than 4.0 (Figure 2). This can be ascribed to the following mechanisms: (1) low oxidation rate of the sulfides, since the amounts of leached sulfate were also low, as in samples 19, 34, 61 and 62. This is in agreement with other authors^{8,30,31} which reported that the rate of sulfides oxidation is decreased by increasing pH of the medium. And (2) As retention by iron (hydr)oxides which precipitate just after sulfide oxidation at high pH, as also reported by several authors.^{16-20,32} The role of iron oxides in arsenic retention by adsorption or co-precipitation is suggested by several authors^{19,33-39} and reveal a mechanism of As concentration in the solid phase as the sulfidic samples are oxidized at slightly acid to alkaline medium.

High oxidation rates were obtained to samples 92 and 93, from Riacho dos Machados, as suggested by the pH drop and high concentrations of sulfur, arsenic and iron in the leachates. The iron mobilization in these samples is due to the low pH range (2.1 to 3.3) of the leachates which favors the dissolution of iron (hydr)oxides and releasing of Fe³⁺ ions.⁴⁰

The rate of sulfides oxidation (e.g. FeS₂ e AsFeS) at pH<2,8 is high due to the catalysis by *Acidithiobacillus ferrooxidans*.^{8,41,42} It is worth pointing out that the mechanism for energy extraction from arsenopyrite by bacteria is favored at pH<2,5. Under such condition, the pH is lower than the point of zero charge (PZC) of the arsenopyrite and the mineral surfaces are positively charged favoring the adhesion of the negatively charged bacterial cells.⁴¹

Correlation coefficients reveal that As leaching is positively correlated to the S and Fe release and negatively correlated to pH (Table 4). Such results corroborate the As release following the acid drainage from arsenopyrite oxidation. Leaching solutions from samples with high pH's presented lower rate of sulfide oxidation and probably precipitation of iron (hydr)oxides in the solid phase. Consequently As was not released from arsenopyrite or was retained by co-precipitation or adsorption onto iron (hydr)oxides inside the columns.

Table 2. Aqueous pH and acid-base accounting (ABA) calculated from potential acidity (PA) and neutralization potential (NP) of the samples

Sample	Type	PA ⁽¹⁾	NP ⁽¹⁾	ABA ⁽¹⁾	pH ⁽¹⁾
19 PT	Overburden	1.15 (± 0.05)	0.35 (± 0.04)	0.80 (± 0.02)	6.63 (± 0.10)
34 PT	Ore	1.48 (± 0.03)	1.08 (± 0.02)	0.40 (± 0.01)	4.78 (± 0.04)
61 SB	Overburden	1.11 (± 0.02)	1.85 (± 0.02)	-0.75 (± 0.01)	8.63 (± 0.02)
62 SB	Ore	1.29 (± 0.02)	1.74 (± 0.02)	-0.45 (± 0.01)	8.37 (± 0.03)
92 RM	Overburden	1.51 (± 0.04)	0.57 (± 0.01)	0.94 (± 0.03)	3.14 (± 0.02)
93 RM	Ore	1.59 (± 0.02)	0.40 (± 0.01)	1.19 (± 0.02)	2.80 (± 0.05)

⁽¹⁾ mean of three replications (±standard deviation)

Table 3. Contents of As, S and As/S ratios in the samples

Sample	Type	As ⁽¹⁾	S ⁽¹⁾	As/S ⁽¹⁾
		mg kg ⁻¹		
19 PT	Overburden	1588 (± 57)	5876 (± 105)	0.27 (± 0.01)
34 PT	Ore	4040 (± 75)	18125 (± 768)	0.22 (± 0.01)
61 SB	Overburden	2524 (± 60)	14872 (± 635)	0.17 (± 0.001)
62 SB	Ore	33133 (± 1528)	71463 (± 691)	0.46 (± 0.02)
92 RM	Overburden	11100 (±238)	101868 (± 1881)	0.11 (± 0.001)
93 RM	Ore	46493 (±857)	422114 (± 5680)	0.11 (± 0.001)

⁽¹⁾ mean of three replications (±standard deviation)

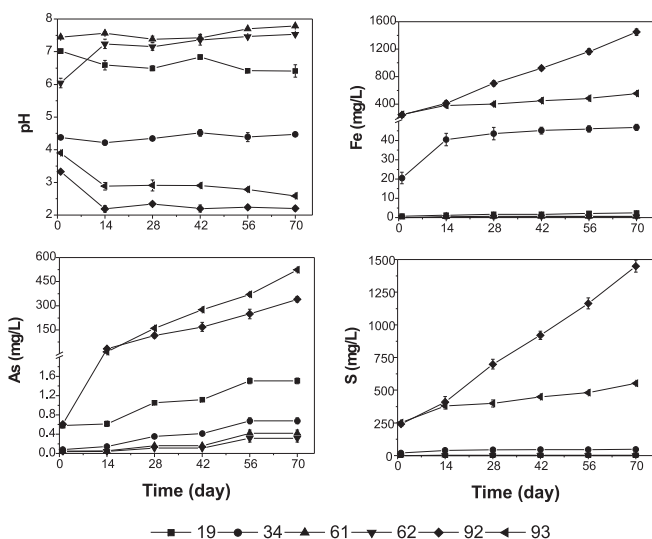


Figure 2. Cumulative amounts of arsenic, sulfur and iron leached from columns and pH variation against time of simulated weathering

Table 4. Correlation coefficients between arsenic, sulfur, iron and pH of the leaching solutions

Variables	S	Fe	pH
As	0.7041***	0.7439***	-0.6258***
S		0.9882***	-0.7798***
Fe			-0.7663***

*** significant at $p < 0.0001$

Our data showed higher acid generation in samples from Riacho dos Machados, followed by samples from Paracatu and finally samples from Santa Barbara with no acid drainage release. Such results, and the tendency for releasing As to the environment, were ascribed to the presence of carbonates, iron (hydr)oxides and the type of sulfides in the samples. Carbonates promoted increase in pH and inhibited sulfide oxidation and As release in samples from Santa Barbara. Such inhibition was ascribed to a decrease in bacterial activity, but it can also be due to microencapsulation of arsenopyrite by iron (hydr)oxides precipitation at the mineral surface as reported by Evangelou.⁴³

CONCLUSION

Oxidation rates were significantly higher in acidic samples ($\text{pH} < 3$) from Riacho dos Machados. Consequently, amounts of Fe and S leached from columns were also higher in these samples. Higher As mobility in acid leachates was ascribed to: higher oxidation rate of arsenopyrite and iron (hydr)oxides dissolution impairing As retention at the solid phase. Presence of carbonates in samples from Santa Barbara decreased the rate of sulfides oxidation and promoted As immobilization. On the other hand, lime added to a partial oxidized sample from Paracatu increased As mobilization.

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