

Characterization of Arsenical Mud from Effluent Treatment of Au Concentration Plants, Minas Gerais – Brazil

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Abstract

The determination of the general properties of arsenical mud was carried out in effluent treatment plant of an Au metallurgical facility, located in Nova Lima, Minas Gerais, Brazil. This effluent, which comes from the calcination stage, is treated via Fe-coprecipitation / lime-neutralization and thus mud with high As concentration is generated. Instrumental methods were applied to investigate physical-chemical characteristics, such as pH, in addition to the forms of occurrence of As and its associations. The results indicated that the mud has an alkaline pH (≈ 8.5), particles with grain size below 20 μm , and As, Fe, S and Al concentrations above 5%. The element As is essentially associated with Fe, Ca, S, and Al, forming phases with wide compositional variation as major and minor constituents generically classified as “complex sulfates” and “compounds with S”. The obtained results could assist optimization of the treatment routes in the plant and even to consider the potential reuse of this arsenic mud as a potential valuable product.

Keywords: Geochemistry and Environmental Mineralogy, Tailings Dam, Arsenic

Introduction

Arsenic (As) is a common deleterious element in gold (Au) deposits (Jacob-Tatapu 2018). Materials with elevated As concentration are difficult to process without the associated environmental risks. Very few facilities in the world are capable of treating material containing high concentration of As. The main sources are sulfides such as arsenopyrite, commonly associated with Au. In the Au metallurgical beneficiation process, stages for treating toxic elements in effluents are essential and corroborate the environmental and social responsibilities of a sustainable mining sector. Due to limited alternatives, the As is often volatilized or left in tailings exposed to lixiviation and are generally arranged in small dams or pits (Deschamps *et al.* 2002; Procópio 2004; Pantuzzo *et al.* 2007a; Bissacot *et al.* 2015; Moura 2015). This fact, coupled with challenges in the mineral industry regarding the sustainability of its

resources and the difficulties of obtaining new environmental licenses, made critical the need for detailed characterization studies in search of new alternatives and improvements for disposal of residues rich in As (Lemos *et al.* 2021a).

The work was focused on arsenical muds generated from the effluent treatment of an Au concentration plant, located in Nova Lima, Minas Gerais (Fig 1). The ore that feeds the plant comes from mines, located within the Rio das Velhas Greenstone Belt in the Iron Quadrangle region and are mainly composed of sulfides such as pyrite, arsenopyrite, pyrrhotite and rare sulfides, like as gerdosffite, galena, sphalerite (Lobato *et al.* 2001; Moura 2015; Kresse *et al.* 2018).

These sulfides are concentrated by flotation, calcined, and subsequently leached to recover Au, as illustrated in Fig 2 (Moura 2015). The As, originating from the sulfide concentrated, is volatilized in the form of As trioxide in the

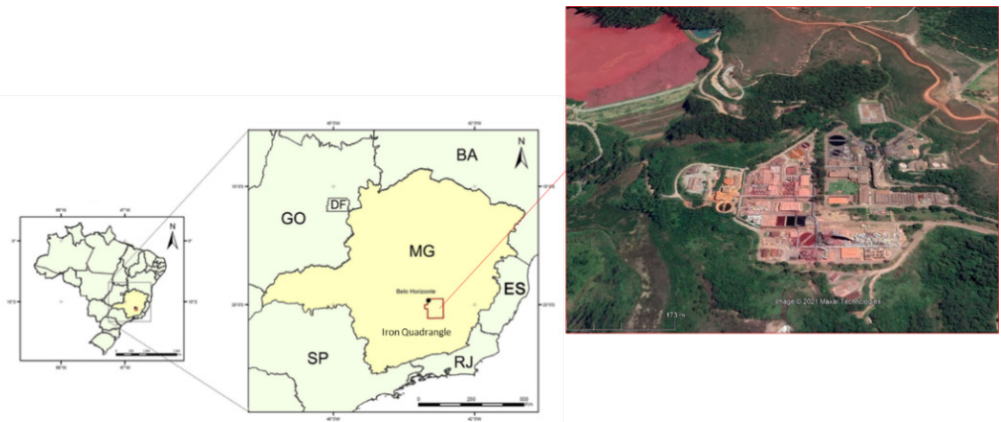


Figure 1 Study area: a. iron quadrangle map location (modified from Ruchkys U.A 2007) and Nova Lima location and b. Nova Lima Metallurgic plant (SIRGAS2000 – 10-09-2019).

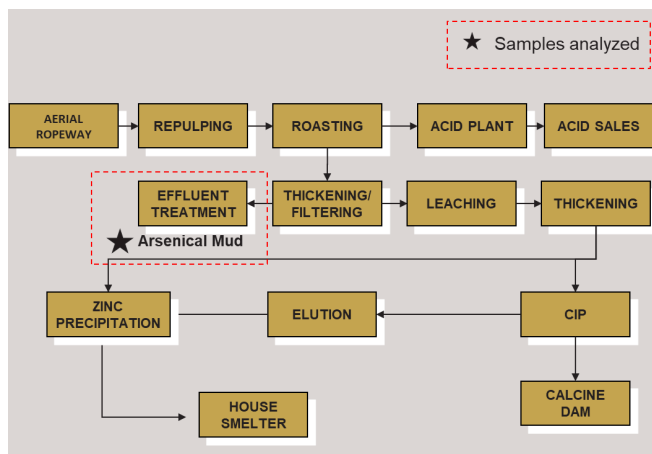


Figure 2 On-going workflow of Nova Lima's plant. The yellow stars represent sampling points in Arsenic effluent treatment (modified from Moura 2015).

roasting stage, absorbed in an aqueous phase in the gas washing towers and finally removed by coprecipitation processes with iron and neutralization with lime (Fig 2). The resulting solid waste (arsenic sludge or mud) is then disposed of in waterproofed ditches (dug into the surface of the land), located in the plant's area of influence (Pantuzzo *et al.* 2007b).

Pantuzzo 2017 refers the presence of As in the waste ditches essentially associated with Fe and to a lesser extent with Ca (probably Ca-arsenates), Al, or even Mn, and Zn, through coprecipitation/adsorption mechanisms. However, it is necessary to detail the sources of As in the waste generated in the plant.

Therefore, the main objective of the present work is the characterization of this current arsenical mud after the neutralization step, mainly the geochemical and mineralogical properties, and identification of the neofomed host phases of As.

Methods

The sampling campaign was performed over twenty-eight days in September 2019 during the production stage, representing a total of 40 samples after neutralization stage from the active plant (Fig 2). All samples were immediately sealed and refrigerated until analysis. Additional material was transferred

to polypropylene bags and frozen until analysis. Refrigerated and frozen samples were packaged and shipped to the chemical laboratory for analysis.

Parameters such as pH of the effluent water samples were obtained using methodologies from the Standard Methods of Water and Wastewater (APHA 2005). Water samples were filtered using a 0.45 µm filter (Sigma Aldrich) and subjected to chemical analysis by inductively coupled plasma mass spectrometry (ICP-MS) at Universidade Federal de Minas Gerais (UFMG) water analysis laboratory.

Chemical analysis of the solid tailings was performed by atomic absorption spectroscopy (AAS using AAS280 FS Varian). Infrared analysis (LECO) was used to obtain analytical S and C data.

The mineralogical study was carried out using polished sections analysed by optical microscopy and scanning electron microscopy (SEM, Field Electron and Ion Company, FEI) at UFMG, Belo Horizonte.

Results and Discussion

This section presents the general properties of the arsenic mud, which in general has particles of fine grain size (P80:15µm).

Geochemistry

The arsenical mud samples are mainly composed of Ca (14.5 - 17.2%), S (13.1 - 13.8%), Fe (6.8 - 8.7%), As (3.6 - 4.2%) and other elements in low concentrations (Tab. 1).

The water has low concentrations of Fe (<2.5 mg /L) and As (1.4 - 5.3 mg/L), which is consistent with the neutralization step in the beneficiation plant. For sulfur, the concentration of 1.0 g/L in the solution of the neutralization step is expected as the pH increases because of the lime addition. The consistency of this information is confirmed, therefore, by the concentration of Fe, As and S found in the solid phase already presented.

Mineralogy

The mineralogical study by SEM revealed the presence of Hematite, Gypsum, Sulfo Arsenical Compounds (CSA), Compounds with S and other elements (Ca, Al, Si, Mg and Fe), Al silicates, Ferrosaponite, Gibbsite

Table 1 Average water pH and concentration of major and trace elements - Solid and Water samples; N – number of samples.

	Solid (N=40)	Residual Water (N=10)
Physical Parameters	Average	Average
pH	-	8.5
Elements	%	mg/L
Fe	8.68	<2.50
As	3.58	5.31
S	13.30	436.39
Si	0.36	-
Ca	14.89	491,01
Al	1.50	<2.50
Mg	0.52	16.58
K	0.02	100.73
Zn	0.43	<0.1
C	0.10	-

Table 2 Mineralogy of Solid samples (average values); N – number of samples.

	Solid (N=40)
Mineral/Composed	Average %
Hematite	1.13
Gypsum (Fe)	28.57
(CSA1 -3%As in composition)	38.36
(CSA2 -13%As in composition)	18.10
(CSA3 -5%As in composition)	11.68
Others	3.03

and Fe / Al oxides. The types of arsenical sulfo compounds (CSA) were differentiated by their As amount, varying from 3 to 13% (Tab 2; Fig 3). In addition to As and S, they are made up of Fe, Al, Zn, Ca.

The arsenical mud consists essentially of "CSA 1" (38.36% by weight), and "Gypsum Fe" (28.57% by weight). The total percentage of all phases with S (sulfates, "Compounds with S" and "CSA") is 90.63% (Fig 3). Also noteworthy are the low amounts of "Hematite", which make up a total of 1.13% by weight in this sample, as well as quartz and other silicate phases classified as others.

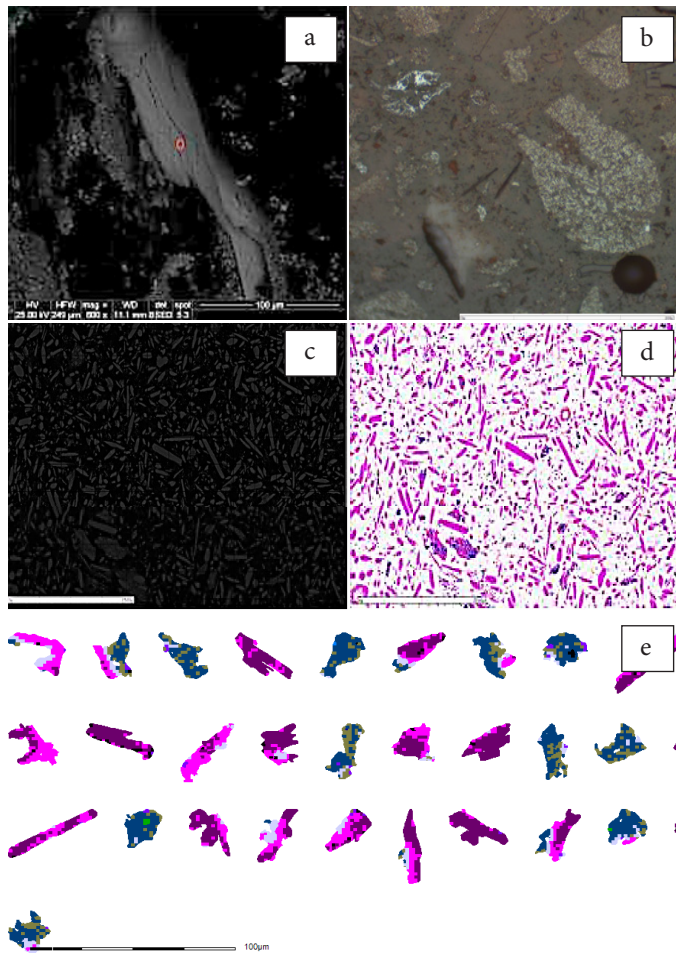


Figure 3 Backscattered electron image of Sulfo Arsenical Compounds in arsenical mud. a) CSA, b) Reflected light image of porous hematite, c) total sample, d) and e) false image of total samples (pink, purple and blue – Gypsum (pink/purple) and CSA (Blue)).

The predominant presence of calcium and sulfur is consistent with the identification of gypsum indicated by electron microscopy (Fig. 3). On the other hand, the occurrence of Fe and As in relevant quantities is associated with the complex phases that contain variable concentrations of As.

The samples underwent several types of “attacks”, from breaking the structure by calcination, followed by complementary chemical processes. This can result in complex phase transformations and, in addition, chemical dissolutions and substitutions in the crystalline structure. As a result, some phases have very complex micro-chemical and textural compositions. These phases with

wide compositional variations and made up of several elements as major and minor constituents were generically classified as “Complex Sulfates”, “CSA”. The rate of this transformation should be directly related to the size of the particles and the availability of the surface for reaction.

In calcination, part of the Fe^{+2} released from the dissolution of the primary minerals (sulfides, oxides, silicates with Fe) is oxidized to Fe^{+3} and precipitated as hematite / oxides, which in turn, may have been attacked chemically generating skeletal and porous hematite, richer in contaminating elements (Fig 3b).

In addition, the breakdown of the structure by calcination may result in ion solubilization,

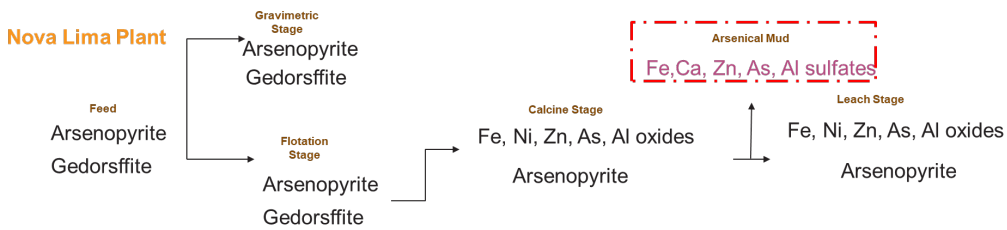


Figure 4 Transformation path of As sources along Nova Lima Au metallurgical plant until neoformation of arsenic mud.

such as Ca and Mg, of some silicates (and carbonates) originally present. Also, the leaching of elements by acidic attacks and the addition of lime and precipitating agents may have caused the precipitation of phases, such as gypsum and other sulfates, dissolution and ionic substitutions, partial to total, resulting in the formation of complex phases, with various constituent elements (e.g., Fe, S, Ca, Mg, Al, Si). Fig 4, therefore, illustrates the transformations of As minerals along the process of this metallurgical plant until the generation of the arsenical sludge.

Conclusions

Arsenical sludge is the product of the neutralization stage of the Au treatment of a plant located in Nova Lima, Brazil. An integrated characterization, including geochemistry and mineralogy was performed to evaluate the sources of As and their associations. The predominant presence of Ca and S is consistent with the identification of gypsum. On the other hand, the occurrence of Fe and As in high quantities is mainly associated with the complex phases with variation in the grades of As.

The arsenical mud is mainly composed by Ca (14.5 - 17.2%), S (13.1 - 13.8%), Fe (6.8 - 8.7%) and As (3.6 - 4.2%). It is noteworthy that the water has low concentrations of Fe (<2.5 mg/L) and As (1.4 - 5.3 mg/L), which is expected after the neutralization step. The samples analysed underwent several types of “attacks”, from breaking the structure by calcination, followed by complementary chemical attacks. This resulted in complex phase transformations and, in addition, chemical dissolutions and substitutions in

the crystalline structure. As a result, some phases have very complex micro-chemical and textural compositions. In the analysed samples, these phases with wide compositional variations and made up of several elements as major and minor constituents were generically classified as “Complex Sulfates”, “CSA”.

From the results of this characterization study, it is possible to propose optimization in the current treatment routes and even propose new alternatives, in addition to initiatives in the reuse of these as a valuable product for As recovery.

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