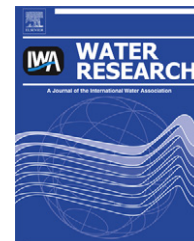


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Arsenic association and stability in long-term disposed arsenic residues

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ABSTRACT

Long-term stability of arsenic residues is investigated by determining arsenic phases remaining in gold mining residues after two decades of impoundment. The residues, generated by arsenic coprecipitation with iron and lime, were disposed of in-lined sites for 9–16 years (pit C) and 16–23 years (pits A and B). Arsenic is present in the residues as As(V) species, predominantly in the form of amorphous iron arsenate (55–75% As_{total} , pits A and B; 55–70% As_{total} , pit C) and sorbed onto amorphous iron-oxyhydroxides (20–33% As_{total} , pits A and B; 22–37% As_{total} , pit C). The presence of minor Ca–arsenate phases (undefined composition) and Al–arsenate coprecipitates is also indicated. The passive enrichment of iron in pits A and B, and the relative low concentration of calcium, sulfur and arsenic if compared to those of pit C, suggest that a soluble Ca–arsenate phase (e.g. $CaHAsO_4 \cdot H_2O$), a fraction of gypsum and As(III) were dissolved along 16–23 years of residue disposal. The presence of As(V) only and excess iron demonstrates the importance of the oxidation state and high Fe/As ratio on long-term stability of arsenic residues.

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1. Introduction

Removal of arsenic from contaminated waters and industrial effluents produces variable amounts of residues, which result in new potential sources of arsenic contamination. Mining and metallurgical activities are important sources of arsenic residues. Established techniques for arsenic removal in these industries often result in generation of large amounts of residues with low arsenic content, thus implying large

disposal costs. More importantly, long-term stability of these residues is still not well understood or fully controlled, presenting potential sources of contamination.

Precipitation with trivalent iron salts and lime (CaO or $Ca(OH)_2$) is a two-step arsenic removal technique that is commonly employed from mining effluents. Arsenic stability (i.e. remobilization) is a matter of debate. Various studies have focused on the potential As release from these residues, using different extracting agents. In a pioneer work, Krause and

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Ettel (1989) determined a solubility below 1 mg/L As (from pH 3 to pH 8 in NaOH/H₂SO₄ aqueous solutions) for Fe(III)–As(V) coprecipitates with iron arsenic molar ratio (Fe/As) \geq 8. By means of leaching procedures, Swash and Monhemius (1995a) observed that Fe(III)–As(V) coprecipitates with Fe/As ratios $>2.3/1$ resulted in an arsenic solubility of approximately 1 mg/L As at pH 5 (acetic-buffered media), which lies in the same order of magnitude of that of scorodite (crystalline FeAsO₄·2H₂O). The solubility of the calcium–arsenate phases (Ca/As molar ratio of 1:1), which varied from 9.2×10^2 to 4.4×10^2 mg/L As, was also determined by these authors. Violante et al. (2007) reported that less than 20% of the total As (As_{total}) was removed by phosphate solutions from various samples of Fe(III)–As(V) coprecipitates, previously aged 30 and 210 days. Multiple leaching agents have been used by Daus et al. (1998) to investigate arsenic release from Fe(III)–As(V) coprecipitates. The authors performed a two-step sequential extraction of Fe(III)–arsenate coprecipitates prepared at approximately pH 7. From 60 to 82% of the total arsenic were extracted with 1 mol/L (sodium hydroxide NaOH) solution from the “iron-hydroxides” present in the samples, whereas the remaining As amount was dissolved with 0.04 mol/L NH₂OH.HCl solution (hydroxylamine).

Most of the reported studies on the solubility of As have been carried out with fresh materials obtained from pure solutions under laboratory conditions. These materials do not reflect both (i) the actual effect of the As sources (i.e. the composition of As-effluents) and reagents (e.g. commercial iron salts/lime) on the nature of the industrial residue and (ii) the effect of disposal site conditions on the ageing processes. Arsenic residues ageing under laboratory conditions do not reproduce the actual long-term behavior in disposal sites. There are also investigations with samples from soil and sediments (Kneebone et al., 2002; Sharif et al., 2008; Paul et al., 2009) and tailings (Paktunc et al., 2003; Mahoney et al., 2005) but these do not represent the residues of As coprecipitation with iron salts and lime produced in the treatment of industrial effluents and water treatment.

Riveros et al. (2001) point out that the long-term stability of arsenic compounds is a function of several parameters, including site characteristics, particle size and crystallinity, presence of oxygen and complexing agents (chloride, organic acids) among others. In a review focusing on As removal as Fe–As coprecipitates with excess Fe, and the stability of these residues under industrial conditions, Harris (2000) states that “... the situation regarding the long-term stability is perhaps not as clear as it appeared to be previously...”. Ritcey (2005) observes the existence of few works focusing on the stability of arsenical residues produced under industrial conditions and submitted to the conditions found in a disposal environment. Therefore, the investigation of arsenic association and its potential mobility from old industrial residues is relevant and contributes to a better understanding of the reported issues.

The Iron-Quadrangle is a historically important and globally known iron–gold geoprovince located in the south-center part of the state of Minas Gerais in Brazil. In the mid-1980s, gold ores from Cuiaba and Raposos mines have been processed in the Queiroz Plant (currently owned by AngloGold Ashanti), in the Nova Lima district. Gold is found along shear zones, hosted in oxide facies and carbonate facies of banded

iron formations (BIFs) (Lobato et al., 2001) and associated mainly with pyrrhotite (Raposos mine) and with pyrite or arsenopyrite (Cuiaba mine) (Vieira, 1991). In the Cuiaba refractory gold ore circuit, gold has been recovered by roasting/carbon-in-pulp (CIP)/cementation; the current throughput is approximately 10⁶ T/year ROM. Minor arsenopyrite (FeAsS) present in the sulfide concentrate is volatilized in the form of arsenic trioxide (As₂O₃) during roasting, absorbed in water in the gas washing towers and, finally, removed by coprecipitation/adsorption with addition of iron salts or oxides and lime. The resulting residues (arsenical slimes) are disposed of in lined pits located in the proximity of the metallurgical plant. The drainage water is collected and recycled to the industrial circuit. Dissolution, reprecipitation, adsorption and recrystallization take place along weathering. One may expect that the less soluble, unstable phases will remain in the pit. By analyzing the residues one may infer the processes that may have taken place along the years of impoundment as well as identify the most stable As-containing phases.

The present work evaluated As association and potential mobility from As residues from Cuiaba metallurgical operation. Samples were collected from three disposal pits designated as A, B and C. Pits A and B (both with 13.500 m³ capacity) were filled from 1987 to 1994, while pit C received residues from 1994 to 2001. The As residues from pits A and B were generated through the *high-lime process*. In this process, the sulfate-rich arsenical effluent (pH 5, 200–300 mg/L As) was neutralized with lime suspension in the two consecutive Pachuca tanks (pH 10 and pH 13, respectively). Iron solution was simultaneously added ((Fe/As)_{wr} ~ 0.4) in the first Pachuca. After sedimentation, the resultant slimes were directed to the disposal pits. A portion of the suspension was recirculated as seed. In the case of pit C, the residues were generated by the *ferrihydrite process* in which arsenic was co-precipitated with Fe ((Fe/As) = 1.3, pH 5) in the first Pachuca tank and neutralized with lime up to pH of approximately 8 (Pachuca-2). The reactions were performed at room temperature.

Long-term stability of arsenic residues was investigated by determining arsenic association with the solid phase's constituents and arsenic potential mobility after two decades of impoundment. A specific sequential extraction protocol (SEP) was developed and optimized with typical arsenical residues from mining operations. Instrumental methods of analysis were applied to confirm the SEP selectivity and also to evaluate arsenic speciation, distribution and current potential mobility from the residues.

2. Materials and methods

A total of 29 samples of As residues were collected from their respective pits (5 from pit A; 3 from pit B; and 21 from pit C) through 11 drilled boreholes (Table S1). The samples were placed in plastic bags and later dried in at 40 °C, homogenized and crushed to pass a sieve mesh size of 180 μm (<80 Mesh Tyler) for chemical analyses.

Bulk samples of the residues were analyzed (dry basis) after microwave digestion in closed vessels, according to an analytical procedure specifically developed for these samples (Pantuzzo et al., 2009). An amount of 100 mg (0.1 mg precision)

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