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Characterization and assessment of chemical modifications of metal-bearing sludges arising from unsuitable disposal

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ABSTRACT

Ettringite–gypsum sludge, formed by neutralization of acid mine drainage with lime, has been stored temporarily in the open pit of a uranium mine that floods periodically. The present study characterized samples of this sludge, named according to the time of placement as Fresh, Intermediate, and Old. Standard leaching and sequential extraction procedures assessed the associations and stabilities of U, Zn, Fe, Mn, and other contaminants in the solid phases. Corresponding mineralogical transformations associated with sludge weathering were modeled using PHREEQC. The main crystalline phases were ettringite, gypsum and calcite; the minor constituents were fluorite and gibbsite. This mineral assemblage could be attributed to the incongruent dissolution of ettringite to form gibbsite, calcite, and gypsum. Sequential extractions indicated high contents of U, Ca, SO_4, and Zn in the water-soluble (exchangeable) and carbonate fractions. Thus, the analytical and modeling results indicated that despite being classified as non-toxic by standard leaching protocols, the minerals composing the sludge could be sources of dissolved F, SO_4, Fe, Zn, Mn, U, and Al under various environmental conditions. Decommissioning strategies intended to prevent contaminant migration will need to consider the chemical stability of the sludge in various environments.

1. Introduction

High levels of metals and associated contaminants in soils, tailings and aqueous wastes from mining activities have been detected extensively around the world. The migration of these contaminants through geological media can result in surface and ground water contamination. The stability of chemical phases in mine wastes during storage is a critical factor because solid wastes may be weathered causing the mobilization of certain contaminants [1–4]. Mining of uranium ore is one of the numerous examples of how improperly disposed mining wastes can release U and associated contaminants to the environment.

From 1970 to 1996, a uranium ore processing mill operating in Caldas Municipality, Brazil, generated tons of tailings and other solid wastes containing sulfide minerals. Sulfide oxidation produced acid mine drainage containing contaminants such as U, Mn, Zn, F, Fe, and SO_4^{2-}. The humid climate of the region intensifies the oxidation and leaching of the tailings. The tailings effluent presently is neutralized with lime $Ca(OH)_2$, producing a high-pH, metal-rich sludge that is disposed into the open pit that floods periodically with acid water. The chemical conditions of the neutralization procedure, i.e., the pH range from 10.5 to 12.0, and the high concentration of ions such as Al^{3+}, Ca^{2+}, OH^- and SO_4^{2-} favors the precipitation of ettringite. The process also promotes the precipitation of metals, including uranium and long term exposure of the sludge to the acidic water could result in dissolution of the precipitates and the remobilization and migration of the toxic elements. Because a liner, such as clay, was not used to prevent leakage or contact between the sludge and acidic pit water, seepage of contaminants from the pit to the groundwater cannot be disregarded.

According to Fernandes et al. [5], the neutralization of the water may be effective in reducing the concentration of the contaminants in the effluent to acceptable limits; however, it is not cost effective. It is also worth noting that the current disposal of the sludge in the open pit may be discontinued in the future pending decisions of the decommissioning process, after being approved by government authorities. Therefore, the characterization of the sludge is essential to the determination of its fate.

The present work is part of a broader project aimed at providing knowledge for the selection of appropriate remediation strategies for decommissioning the Caldas mine. This paper investigates the potential release of contaminants from 3 different samples of sludge disposed at the mine; it also describes mineral transformations that could result in contaminant release. The chemical and mineralogical characterization of the sludges, their classification as toxic or non-toxic material, and sequential extraction are

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presented in order to provide insights into the chemistry of the metal-bearing sludges. Finally, geochemical modeling is used to simulate the chemical reactions that may result from the interaction between the sludge and acidic water at the disposal site.

2. Methods

2.1. Solid samples

Samples were identified as Fresh sludge (sampled from the neutralization tank at the Water Treatment Station), Intermediate sludge (sampled from the mine opening where it has been disposed since 1996) and Old sludge (sampled from an old deactivated dam that was used for disposal, before 1996). Samples of different ages were chosen in order to investigate if changes in environmental conditions could affect metal availability and/or mobility. Samples were provided by Indústrias Nucleares do Brasil.

2.2. Characterization of the samples

X-ray diffraction was carried out for mineralogical characterization and for semi-quantitative mineralogical estimation. This technique was also used to identify the crystalline phases of the residues following steps A and B of the sequential extraction procedure in order to prove the effectiveness of the extraction process. After step C the amount of remaining sample became insufficient for this determination. Samples were run with a semi-automatic Rigaku diffractometer (model Geigerflex) with slit fixed at 40 mm/min and CuKα monochromatic radiation at a speed of $8^\circ 2\theta$/min (4–70°). Working conditions were 30 mA and 40 kV. Atomic absorption spectrometer (AAS) analyses were carried out using a Varian spectrometer (model AA240FS) after the digestion of the sample for determination of non-radioactive elements. Uranium analyses were carried out using a Kevex Ray spectrometer (model Sigma X9050), coupled with a radioactive source of americium (Am^{241}) and a Si(Li) detector. The specific surface area was measured by the BET method multiple point technique (Quantachrome Corp., Nova 2200 equipment).

2.3. Standard leaching procedures

Standard leaching procedures [6,7] were used to classify the samples as toxic or non-toxic as well as inert or non-inert. The ABNT NBR 10005:2004 [6] procedure consisted of agitating the solid in a buffered acetic acid solution at pH 4.93 for 18 h. The solid/liquid ratio was 1:20. After agitation, the suspension was filtered and analyzed for the selected elements. The ABNT NBR 10006:2004 [7] procedure consisted of wetting 250 g of dry solid sample with 1L of distilled water without agitation for 7 days. Afterward, an aliquot was filtered and analyzed for the selected elements using atomic absorption spectroscopy (AAS) (Varian model AA240FS) and ICP-MS spectrometry (PerkinElmer, Elan 9000 model). Both procedures could be interpreted to indicate the maximum allowable concentration for the elements in solution.

2.4. Sequential extraction

Sequential extraction was used to identify constituents of the crystalline and amorphous phases and their stabilities under different environmental conditions. The elements U, Ca, Al, Mn, Fe, Zn, F were chosen due to the high concentrations in the solid samples and/or because of their hazardous character. Five extraction steps were utilized based on Pantuzzo and Ciminelli [8].

2.4.1. Step A—soluble in de-ionized water

1.0 g of each sludge (dry basis) was introduced into a 1000 mL beaker containing 850 mL of de-ionized water with mechanical stirring for 24 h, then, the solution was filtered using a 0.45 μm Millipore filter. The liquid phase was diluted to 1000 mL with de-ionized water then analyzed for metals by AAS. The solid was dried at 40 °C for 6 h and used in the next step.

2.4.2. Step B—calcium carbonates, calcium oxides and exchangeable ions

The solid remainder from step A was extracted using 25 mL of 1 mol/L sodium acetate buffer solution at pH 5 (adjusted by acetic acid) for 5 h in Marconi Rotary Agitation Apparatus (model MA 160/8P), capable of end-over-end rotation at 60 rpm at room temperature.

2.4.3. Step C—amorphous Fe/Mn oxy-hydroxides

The residue from step B was extracted with 25 mL of 0.4 mol/L NH_2OH in 0.25 mol/L HCl solution for 1 h under agitation in horizontal shaker at 50 °C.

2.4.4. Step D—crystalline Fe/Mn oxy-hydroxides

The residue from step C was extracted with 25 mL of 4.2 mol/L HCl + 6.6 g/L ascorbic acid + 8.82 g/L sodium citrate solution at 80 °C for 2.5 h in horizontal shaker.

2.4.5. Step E—residual

The residue from step D was totally dissolved by acid digestion (10 mL HCl + 10 mL HF + 5 mL HNO_3) in teflon beaker at 150 °C in order to vaporize all gases and reduce the volume of solution. 5 mL of HCl was added to the final solution and it was cooled at room temperature

The solutions from steps B to E were obtained by centrifugation and filtration, through a 0.45 μm Millipore filter. The final volume was diluted to 100 mL with de-ionized water and then analyzed for U, Fe, Al, Mn, Ca, $SO_4{}^{2-}$, Zn and F^- by AAS, Energy-dispersive X-ray spectrometry (Kevex Ray spectrometer – model Sigma-x 9050), barium sulfate turbidimetry (UV Visible Varian Spectrophotometer – model Cary 50) and potentiometric determination by ion selective electrode method.

2.5. Modeling the dissolution of ettringite in the acid water at the Pit Lake

The mineralogical transformations that may take place in the pit, where the Intermediate sludge is periodically exposed to acidic water, were modeled using the PHREEQC geochemical program. PHREEQC is a speciation and reaction path modeling program that can simulate many different chemical reactions including dissolution-precipitation reactions, mixing of solutions and water evaporation [9]. The interactive version of the program (PHREEQCI) was used in this work to construct forward models to evaluate if the incongruent dissolution of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) in the acidic systems could feasibly produce basaluminite ($Al_4(OH)_{10}SO_4$), gibbsite ($Al(OH)_3$), gypsum ($CaSO_4\cdot 2H_2O$), and/or bassanite ($CaSO_4\cdot 0.5H_2O$). The models also were used to indicate the corresponding effluent associated with these phase transformations. The thermodynamic properties of basaluminite were taken from the WATEQ4F data base [10] and added to the LLNL data base [11] and used in the PHREEQC simulations. Uranium and other trace metals were not used in the simulations because the XRD data do not include the identification of minerals of those metals.