# 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.

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## 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 $8°2\theta$/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 1 L 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 ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O$) in the acidic systems could feasibly produce basaluminite ($Al_4(OH)_{10}SO_4$), gibbsite ($Al(OH)_3$), gypsum ($CaSO_4\cdot2H_2O$), and/or bassanite ($CaSO_4\cdot0.5H_2O$). 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.

**Table 1**
Chemical composition of the treatment sludges samples determined by wet analyses, and specific surface area.

| Analysis | Fresh (%) | Intermediate (%) | Old (%) |
|---|---|---|---|
| Loss of ignition | 31.2 | 30.5 | 35.4 |
| $U_3O_8$ | 0.24 | 0.68 | 0.58 |
| $ThO_2$ | 0.01 | 0.04 | 0.04 |
| $MnO_2$ | 3.8 | 4.3 | 1.5 |
| CaO | 33.8 | 28.8 | 30.4 |
| $SO_3$ | 18.3 | 12.1 | 14.8 |
| $Fe_2O_3$ | 0.5 | 1.9 | 7.7 |
| F | 1.5 | 2.50 | 0.7 |
| ZnO | 0.5 | 0.83 | 0.6 |
| $Al_2O_3$ | 6.40 | 14.7 | 4.5 |
| $SiO_2$ | 0.9 | 2.1 | 2.8 |
| MgO | 2.8 | 1.6 | 1.0 |
| Specific surface area ($m^2/g$) | 16.55 | 134.24 | 34.90 |

Loss of ignition = humidity, carbonates, organic matter, water of hydration.

## 3. Results and discussion

### 3.1. Mineralogical and chemical characterization

Minerals identified by XRD indicate the predominant crystalline phases (>50%) were ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O$) in the Fresh and Old sludges and gypsum ($CaSO_4\cdot2H_2O$) in the Intermediate sludge (Fig. 1). Minor phases (<5%) were calcite ($CaCO_3$), anhydrite ($CaSO_4$), bassanite ($CaSO_4\cdot0.5H_2O$).

Chemical analysis of the treatment sludges (Table 1) shows the Fresh, Intermediate, and Old sludges consist mostly of Ca and S, due to the lime treatment of the acid mine drainage. The high loss of ignition (>30%) is mostly due to the water of hydration of ettringite and gypsum; also owing to the presence of calcite. It is also observed that U content of the sludge varied from 0.24% to 0.68%, which is higher than in the majority of the current uranium ores [12]. The elements Fe, Mn, Al, Si, F, Mg, and Zn were also detected. Besides U, Mn, Zn, and F are the main constituents of concern because of their toxicity or their high content in the samples [13].

The main difference among the three samples is the predominance of gypsum in the Intermediate sludge, which may be related to the dissolution of ettringite in periodic contact with acidic water in the mine opening. According to Myneni et al. [14] ettringite is a stable mineral at pH above 10.7. However, below neutral pH, ettringite could decompose by incongruent dissolution to gypsum, Al-hydroxides, and Al-hydroxy sulfates. The former authors identified some poorly crystalline phases such as Ca–Al-hydroxy sulfate (jurbanite and basaluminite), gypsum, and Al-hydroxide at pH < 5. In the present work, no Ca–Al-hydroxy sulfate crystalline phases of any kind were identified.

Ettringite has the ability to incorporate and immobilize critical metallic pollutants, cationic and anionic species, in its crystal lattice, which may contribute to attenuation of pollutants [15,16]. As ettringite is one of the most prevalent crystalline phases in the sludges, it was hypothesized that it could act as a reservoir for the U and other metallic components. Therefore, probable dissolution of ettringite due to the contact with the acid medium for a long period could release contaminants to the environment. On the other hand, according to Ribet et al. [17] the importance of gypsum as a trace metal host is unclear, but may be relatively minor.

Specific surface area, shown in Table 1, is greater for the Intermediate sample, 134.24 $m^2/g$, compared to the others 16.55 $m^2/g$ (Fresh) and 34.90 $m^2/g$ (Old). High specific surface area implies a more reactive material capable of ion exchange or even adsorption of metals. Other properties such as bulk density, porosity and equivalent diameter were also analyzed for the Intermediate sludge, assaying 0.69 g cm$^{-3}$, 78% and 0.13 mm, respectively.

### 3.2. Classification

The ABNT NBR 10004:2004 [18] standard procedure was used to classify the samples as toxic or non-toxic. The soluble concentrations of all elements assessed (As, Ba, Cd, Pb, Cr, F, Hg, Ag, Se, Cu, Fe, Al, Zn, Mn, Ca, $SO_4^{2-}$) did not exceed the upper threshold permitted limit and the samples were classified as non-toxic. As the samples were classified as non-toxic, they needed to be classified as inert or non-inert. Using the ABNT NBR 10005:2004 [6] procedure, the samples were classified as non-inert because soluble concentrations of sulfate (1590–1870 mg/L) and fluoride (4.3–7.0 mg/L), were found to exceed concentrations set by the standards procedure (e.g. 250 mg/L for sulfate and 1.5 mg/L for fluoride). With regard to the other aforementioned elements, no threshold values have been exceeded. This is explained by the high pH (around 8) of the final solution, which favors the precipitation of the majority of the contaminants as hydroxides.

Since the sludges were classified as non-inert they cannot be disposed in the environment without precautionary measures as inappropriate disposal permits the contaminants to spread into soil, sediments, surface water and ground water. In a study about human health risk screening of contaminants in Caldas mining, the chemical toxicity of some non-radioactive and radioactive contaminants such as Mn, F, and U was of greater concern, despite the fact that in this facility most of the attention was focused on radiation risks [19].

Radioactive isotopes, such as ^{210}Pb, [226]Ra, [228]Ra, also alfa (total) and beta (total) counting, were also determined (data not shown). All samples were below the clearance values according to PR 3.01/001 [20] which is set at 10,000 Bq/kg for [226]Ra and [228]Ra and 1,000 Bq/kg for [210]Pb. However, the Brazilian Nuclear Committee (CNEN) determines that, in case involving great amount of material containing natural radioactive or technically modified substances, the clearance values must be determined for each individual case.

### 3.3. Sequential extraction results

Sequential extraction procedures utilize progressively more destructive reagents to provide insight into the association of the solid phases and trace elements [3,4,21,22]. The sequential extraction results for the sludge samples indicated an extraction efficiency of more than 90% for all the analyses of metal partitioning between the components of the sludges. The procedure comprised 5 steps. Step A determined the water soluble elements, mainly sulfates. Step B extracted exchangeable ions, calcium carbonates and oxides. Step C extracted amorphous oxyhydroxides, especially ferric iron and manganese. Step D extracted metals linked to specific crystalline oxides, mainly iron. Finally, step E was carried out in order to dissolve the final residue of the sample and to provide the mass balance of the system. The extraction data for the selected elements are depicted in Fig. 2 and the discussion of the results of the sequential extraction for each element is described below.

#### 3.3.1. Uranium

As a consequence of the liming of the acid water, U can be precipitated as calcium diuranate $CaU_2O_7$, but it could also co-precipitate or be adsorbed on the surface of carbonates and ferric oxides [23]. The precipitation of uranium as calcium diuranate can be described by the following reaction:

$$2[UO_2(SO_4)_3]^{4-} + 3Ca(OH)_{2(aq)} \rightleftharpoons CaU_2O_{7(s)} + 2CaSO_{4(s)}$$

$$+ 3H_2O_{(l)} + 4SO_4^{2-} \tag{1}$$
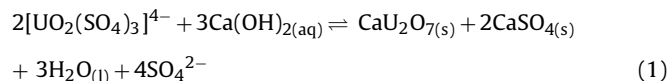
According to Fig. 2 most of the U is extracted in step B, which implies its association with carbonate (calcite) or calcium oxide ($CaU_2O_7$) fractions or as exchangeable ion. However, it could be
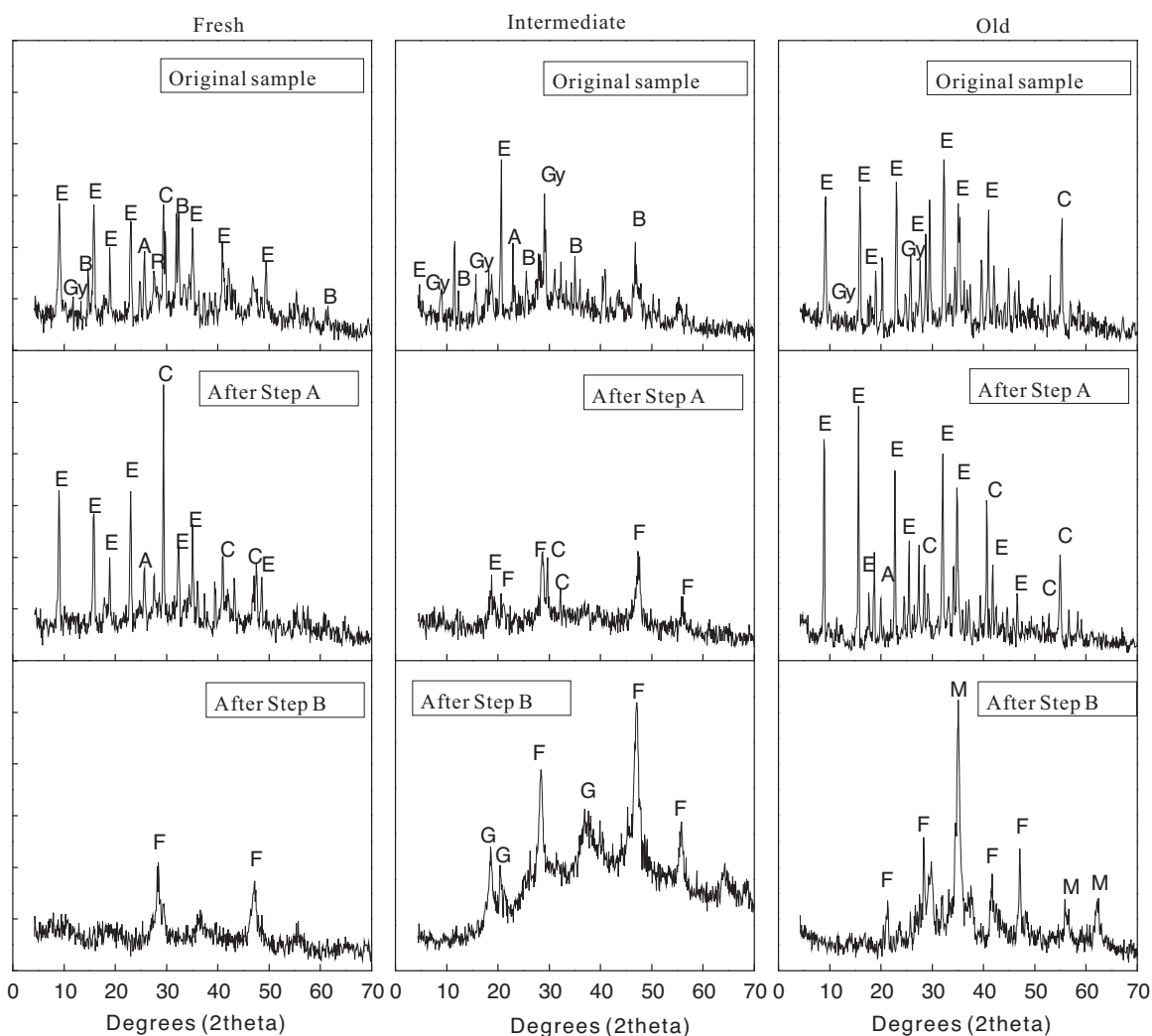
**Fig. 1.** XRD patterns of the Fresh, Intermediate and Old samples. Original sample, after step A (water soluble) and after step B (extraction with NaOAc/HOAc). E = ettringite, Gy = gypsum; B = bassanite; A = anhydrite, C = calcite; F = fluorite; G = gibbsite; M = magnetite.

noted that with respect to Intermediate sludge, uranium extraction was also particularly relevant in step A, around 20%, which is related to the soluble fraction. The authors believe that the soluble U extracted during step A for the Intermediate sample did not come from the dissolution of $CaU_2O_7$ because calcium diuranate was also present in the Old sample of similar content. The greater solubility of U presented by the Intermediate sample might be due to modifications occurring over 15 years of storage in contact with the acid water. The modifications might involve the dissolution of minerals such as ettringite and the consequent release of associated anionic and cationic contaminant species [16]. It is important to emphasize that the dissolution of U, mainly in steps A and B, which is considered the most labile fraction, reinforces the need for careful disposal of the Intermediate sludge which means the construction of an appropriate place having layers to prevent seepage.

Previous studies using sediments, contaminated soils and sludge, show similar results to those reported in the present work. Martin et al. [24] found 60% of uranium in the exchangeable phase in river sediment contaminated by mining activities. Crespo et al. [23] in a investigation about U distribution in granitic fracture fillings pointed out that due to rock–water interaction, uranium is mainly precipitated as mineral phases and/or coprecipitated with carbonates. Choy et al. [25] in a study about chemical leaching of

depleted U from contaminated soils showed that 20–40% of the total U may be attributed to the carbonate fraction, 8–26% to Fe and Mn oxides, and 16–28% to organic matter. The results indicated that the leachability of U was low since none of it was removed in exchangeable fraction. Francis and Dodge [26] showed that 50% of the total U present in one sludge generated in U production was associated with the carbonate fraction, followed by 17% in the exchangeable fraction. Winderlund et al. [22] used sequential extraction procedure to assess metal release from a calcite–gypsum sludge formed in a flooded tailings impoundment. The extracted carbonate and oxide fractions contained >97% of the total amount of Cd, Co, Cu, Ni, Pb and Zn in the sludge, which seems to come from sorption and/or coprecipitation reactions on the surfaces of calcite and Fe, Al and Mn oxyhydroxides. However, the former authors pointed out that cationic metals once remobilized from dissolving calcite, gypsum and also Al oxyhydroxides could be readsorbed onto Fe oxyhydroxides remaining stable under oxidizing conditions.

### 3.3.2. Calcium

Fig. 2 shows that the extraction of Ca occurred primarily in step A (47–38%) indicating its association with soluble sulfates. In step B, 43–20% of Ca was dissolved suggesting its association with carbonates and calcium oxides. The crystalline phases, such as bassanite
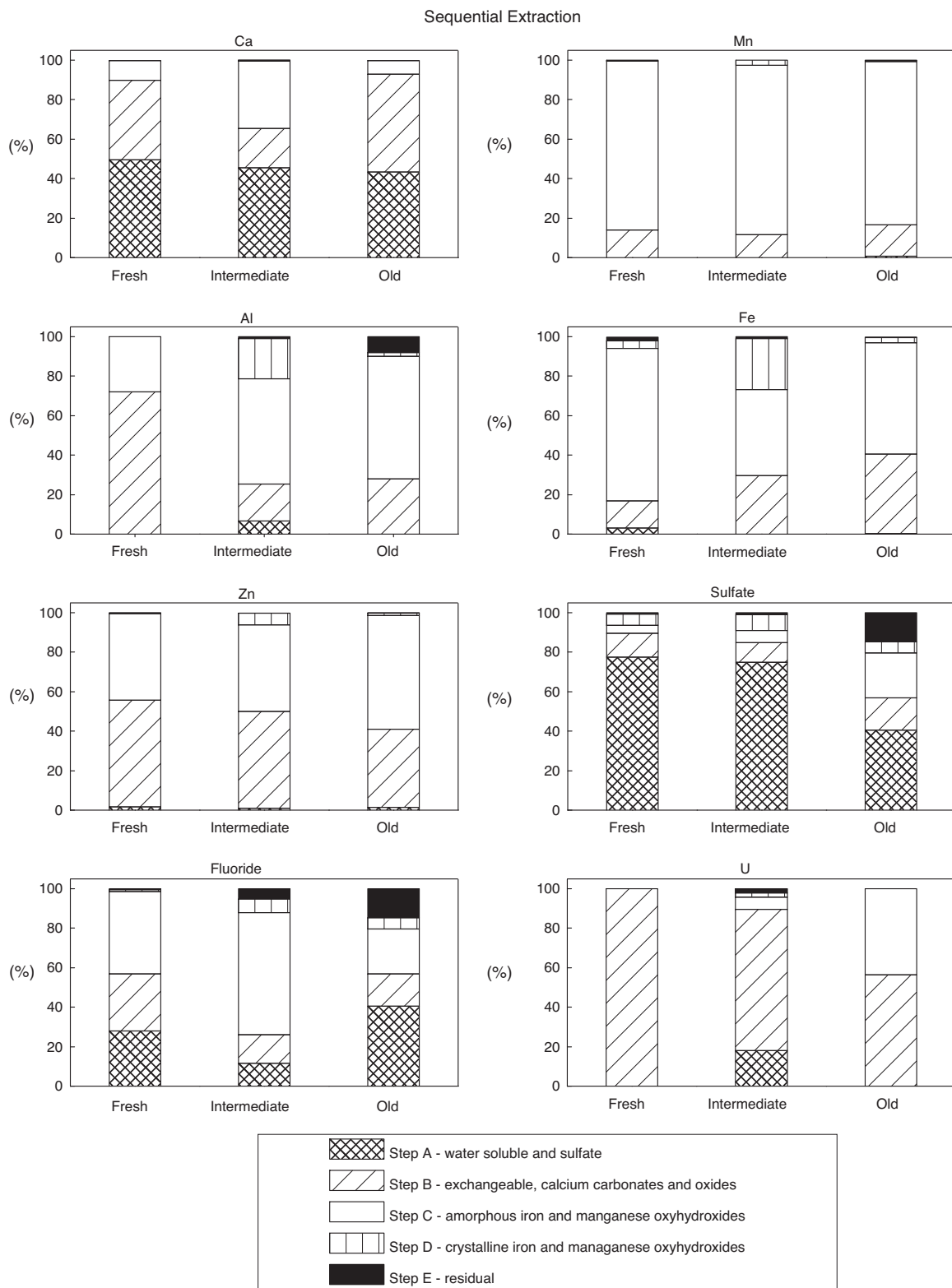
Sequential Extraction



**Fig. 2.** Sequential extraction results for Ca, Mn, Al, Fe, Zn, sulfate, fluoride and U of each of the sludges.

(B), gypsum (Gy), calcite (C) and ettringite (E), initially present in the original samples, contain calcium sulfate and carbonate and, as shown by X-ray diffraction in Fig. 1, these phases were dissolved in steps A and B. After steps A and B, new crystalline phases were highlighted. For example, after the dissolution of the gypsum and bassanite in step A, it was possible to identify other crystalline phases in the Intermediate sample that were not previously identified in the original sample, such as calcite and fluorite. However, it was verified that more than 70% of the sample consists of amorphous material. For the Intermediate sludge, a significant amount of Ca (35%) was also extracted in step C, indicating its association with an amorphous phase not identified in the present study.

### 3.3.3. Iron, manganese, zinc

The elements Fe, Mn, and Zn were largely removed in steps B and C, which comprise the dissolution of carbonates and amorphous oxides, respectively. According to Fig. 2, step B, the content of iron as carbonate increases with the aging of the samples, as the highest content is present in the Old sample (40%) followed by Intermediate (29%) and Fresh (14%). This is indicative of the absorption of $CO_2$ during weathering of the initially high-pH samples [27]. The Fe in the samples, associated with amorphous oxides, varied from 43% to 77%, with the Fresh sample presenting the higher content. A significant content of Fe as crystalline oxides (25%) was verified only for the Intermediate sludge. The presence of Fe as a crystalline oxide is not well understood. However, what is suggested is that amorphous iron changed to crystalline iron over the years because of complex chemical condition of the disposal site. Manganese is predominantly associated with amorphous oxides, 76–85%, dissolved in step C. Zinc is associated with Mn and Fe carbonates and amorphous oxides. The fact that iron, manganese and zinc minerals are mostly as amorphous, explains why the corresponding minerals were not identified by XRD.

### 3.3.4. Aluminum

The moderate acidity from step B (final pH around 5) enhanced ettringite dissolution and the consequent release of aluminum and calcium, especially for Fresh sludge. The results of XRD depicted in Fig. 1 show that after step B the ettringite phase is no longer present. However, most of the aluminum from Old and Intermediate samples was dissolved in the following step C, which may also come from amorphous Al-hydroxides from the samples, not identified by XRD. It is observed from Fig. 1 that the Intermediate sludge displays a different pattern since it is the only sludge that presents the mineral gibbsite after the extraction step B. Gibbsite, which is a crystalline aluminum oxide and is soluble only in very acidic conditions, must have been dissolved in step D as the pH of this step is less than 1. As step D extracts crystalline phases, it was conclude that the soluble Al from step D (18.3%) comes from the dissolution of gibbsite formed during the contact of the acid water with the Intermediate sludge in the open pit. The presence of gibbsite, which may be explained by Eq. (2) item 3.5, was confirmed by the X-ray diffraction shown in Fig. 1 and corroborates the fact that Intermediate sludge is not inert and undergoes modifications. Step E is responsible for the dissolution of silicates, including aluminosilicates.

### 3.3.5. Sulfate

The sulfate was dissolved predominantly (73.6%) in step A, indicating the dissolution of gypsum and other soluble sulfate minerals. XRD of the residual solids after step A for all samples (Fig. 1) show that gypsum was completely removed during the initial step. In steps B and C, sulfate comes from the dissolution of ettringite and other amorphous sulfates which were not extracted in step A. The high solubility of sulfate is in agreement with the results obtained using ABNT NBR 10005 [6] procedure, which classified the samples as non-inert material.

### 3.3.6. Fluoride

The significant content of dissolved fluoride in steps A and B, especially for Old (40% and 16%, respectively) and Fresh (27% and 29%, respectively) sludges, suggests that this element is present as soluble amorphous phases that are not identifiable by the X-rays diffraction. Similar to sulfate, the high solubility of fluoride conferred the classification of non-inert material to the sludges. However, the majority of fluoride was extracted in step C (20–52%) and must be due to the dissolution of the fluorite ($CaF_2$). Fig. 1 shows the presence of the crystalline fluorite after step B for all samples. Fluorite is soluble in very acidic pH, which is consistent with the experimental conditions of steps C–E whose final pH is below 1. Therefore, it is unlikely that fluoride extracted in steps A and B is due to the dissolution of fluorite; it is more likely that it came from the dissolution of an amorphous soluble form.

### 3.4. Modeling the dissolution of ettringite in the acidic waters of the Pit Lake

According to XRD, ettringite is the main mineral formed in the treatment of AMD waters at Caldas uranium mine. However, the sludge deposited in the Pit Lake can be flooded seasonally by acidic water and undergo partial dissolution. To model this incongruent dissolution process, the reaction-path modeling program PHREEQC was used. Forward equilibrium models were constructed to dissolve one mol of ettringite in 1 L of water with the Pit Lake composition, and the resulting solution evaporated until the precipitate dried. This process was intended to simulate the intermittent flooding of the precipitate during the rainy season and subsequent evaporation during the dry season. The composition of the water used in the simulation of the dissolution of ettringite is given in Table 2. It represents the water that floods the Intermediate sludge every rainy season and was collected closer to the area were the sludge was stored.

Before the results of the simulations are presented, it should be explained that the minerals that were allowed to precipitate are the main minerals observed in the XRD results: ettringite, calcite, gibbsite, bassanite, and gypsum. The minerals gypsum and ettringite appear in detectable concentrations in the original three sludges, calcite in the Fresh and Old sludge, and bassanite in the Fresh and Intermediate sludge. Basaluminite was initially included in the models because other authors have reported the presence of aluminum hydroxyl sulfate related to the weathering of ettringite in acidic systems [14]. However, if both basaluminite and gibbsite are allowed to precipitate in the simulation, only gibbsite precipitates, because it is less soluble than basaluminite. If gibbsite is not allowed to precipitate, then basaluminite forms. Although gibbsite was not detected in the original samples, it was detected in residual solids after extraction with NaOAc/HOAc. In the modeled reactions, the saturation indexes of the minerals ettringite, calcite, gibbsite, bassanite, and gypsum were equal to zero (equilibrium between the mineral and solution) allowing the mineral to precipitate if the solution becomes supersaturated with respect to the mineral. The validation of this modeling work relies on the comparison of the minerals formed in the model exercise with the minerals that are observed in the XRD results.

In Fig. 3A the composition of the precipitate after each addition of ettringite (10 steps to add 1 mol) is presented, evaporation of the water has not occurred yet. Carbon dioxide was allowed to dissolve up to 2.5 mol/L of solution (equivalent to atmosphere of pure $CO_2$). After the addition of only 0.1 mol of ettringite the solution did not precipitate any minerals and the pH was still low. However, after the addition of 0.2 mol of ettringite, the minerals calcite, gibbsite, and gypsum reached equilibrium and began to precipitate. The proportion of these minerals in the precipitate remained constant up to the addition of 0.9 mol of ettringite. The pH of the solution was buffered to 7.7 by this mineral assemblage. For the last step, after addition of 1.0 mol, ettringite reaches equilibrium with this mineral assemblage but at expenses of a decrease in the fraction of calcite, gibbsite and gypsum. Bassanite was not formed during the simulated dissolution and precipitation process.

The composition of the precipitate after water is evaporated from the system is presented in Fig. 3B. The composition depends on the amount of $CO_2$ that is allowed to dissolve in the system. If no inputs of $CO_2(g)$ are modeled, ettringite forms again after mixing with the acidic water and evaporation of the solution. As

**Table 2**
Composition of the acid water.

| Parameter[a] | $T(°C)$ | pH | Al | Mn | Zn | Ca | Mg | K | Si | Sr | Fe | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acidic water | 24.3 | 2.7 | 106 | 34 | 7.3 | 95 | 5.9 | 9.5 | 17.4 | 2.2 | 35.5 | 1000 |

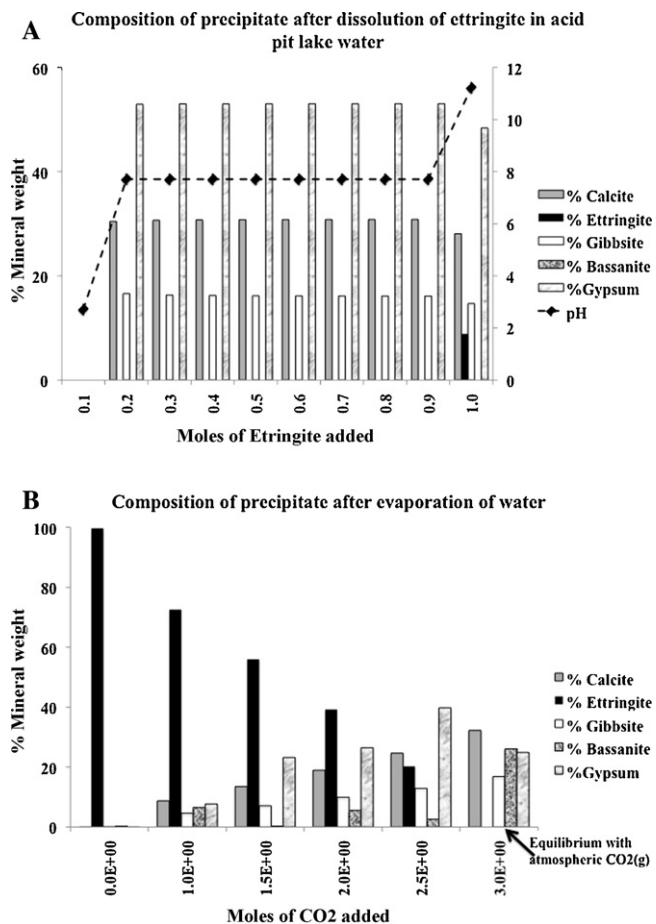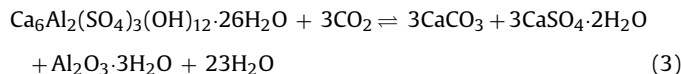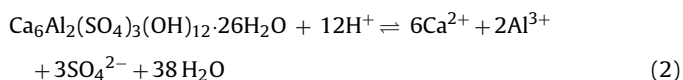[a] Unless otherwise specified, the values are in mg/L, except pH and temperature.



**Fig. 3.** (A) Evolution of precipitate as 1 mol of ettringite is dissolved in the acid Pit Lake water in 10 steps. (B) Mineralogical composition of dry precipitate formed as 1 mol of ettringite is dissolved in lake pit water and evaporated. After evaporation, if no inputs of $CO_2(g)$ are modeled, ettringite is formed again. As $CO_2(g)$ is introduced in the system, ettringite dissolves and forms other minerals such as calcite, gypsum, gibbsite, and bassanite after evaporation. After evaporation, the highest concentration of bassanite and lowest ettringite in the solid occur in system in equilibrium with atmospheric $CO_2$.

$CO_2(g)$ is introduced into the system, ettringite is present but the minerals calcite, gypsum, gibbsite, and bassanite are formed. The highest percentage of bassanite and lowest percentage of ettringite in the solid occur in system in equilibrium with atmospheric $CO_2$. The acidic waters that flood the Intermediate sludge promote the formation of bassanite and decrease the concentration of calcite in the final simulated sludge. As observed in the XRD results, ettringite is less abundant in the Intermediate sludge.

According to the simulation for the Intermediate sludge, the situation is: first ettringite dissolves forming the minerals calcite, gibbsite, and gypsum as the dissolution of ettringite proceeds, and finally reaching equilibrium with ettringite when the dissolved ettringite reaches 1 mol/L or more. The reactions that could explain these processes are:

$$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O + 12H^+ \rightleftharpoons 6Ca^{2+} + 2Al^{3+}$$
$$+ 3SO_4^{2-} + 38 H_2O \tag{2}$$

$$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O + 3CO_2 \rightleftharpoons 3CaCO_3 + 3CaSO_4 \cdot 2H_2O$$
$$+ Al_2O_3 \cdot 3H_2O + 23H_2O \tag{3}$$

Bassanite does not form during the dissolution of ettringite in the acid water. This mineral forms by dehydration of gypsum when water is evaporated from the sludge, i.e. during the dry season.

$$CaSO_4 \cdot 2H_2O \rightleftharpoons CaSO_4 \cdot 0.5H_2O + 1.5H_2O \tag{4}$$
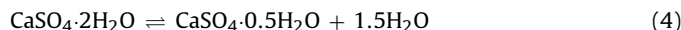
The results of the simulations suggest that the composition of the sludge depends strongly on the interaction with acidic water and atmospheric $CO_2$. It should be noted that there are some limitations to the modeling, such as: (1) The model considers equilibrium conditions for the formation of the minerals in each modeled step. It is possible that the reactions are not fully equilibrated in the real system. (2) One cycle of dissolution of ettringite and drying of the precipitate has been modeled. In the real system repeated cycles of wet and dry seasons could change the relative composition of the mineral assemblage, and (3) different amounts of $CO_2$ have been added to the system to simulate the interaction with atmospheric $CO_2$. However, the real $CO_2$ additions to the system are unknown. Even having these limitations, the results of the simulations show the importance of the location and exposure of the sludge to other fluids and the importance of modeling the possible processes occurring during the disposal of uranium waste and treatment of acid mine drainage from similar sites.

## 4. Conclusion

The present study evaluated the mineralogy and chemistry of Fresh, Intermediate, and Old sludge produced by the neutralization of acidic effluent with lime. The similarities and differences among the samples were attributed to the specific environmental conditions to which they were exposed. The samples consist mainly of ettringite and gypsum. Chemical composition of the sludge was dominantly Ca and S with lesser amounts of Mg, Mn, Al, Fe, Zn, F, Si, and U. Although all the sludges were classified as non-inert on the basis of standard leaching tests, they could be a source of soluble fluoride and sulfate. However, Intermediate sludge is more chemically unstable if compared with the others. The sequential extraction procedure showed that, specifically for this sludge, U, F and sulfate are present in the labile fraction; consisted mainly of steps A and B. Its chemical instability owes to a combination of factors such as weathering and acid mine water in the site, which has caused the dissolution of ettringite and the release of associated contaminant elements. Another characteristic of the Intermediate sludge, which may be associated with the transformations occurred in the disposal site, is its large surface area; almost 10 times greater than the others.

The assessment of the modifications suffered by the Intermediate sludge arising from unsuitable disposal is an alert to the industry to the possibility of migration of the contaminants from the unlined open pit to the ground water. Therefore, the decommissioning strategy should take this chemical instability into consideration when building an appropriate disposal site to prevent seepage. Otherwise, if the current situation remains, it can pose risks to the environment. The results of the simulations show the importance of the location and exposure of the sludge to other liquids as well

as the importance of modeling the possible processes occurring during the disposal of uranium waste and treatment of acid mine drainage from similar sites.

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