

Estimation of Potential Pollution of Uranium Sludge from Acid Water Treatment

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Abstract

In southeastern Brazil, a closed uranium mine produces acid mine water at pH 2.7 which contains significant concentrations of uranium and other elements like manganese, sulfate, iron and zinc. The contaminants are removed from the acid water to acceptable limits through precipitation of the elements using lime. The precipitation procedure has been used for more than fifteen years and generates a sludge which is disposed of into the mine opening. The present study consists of the characterization of different samples of the sludge and their classification according to leaching standard procedures in order to assess the resolubilization of the contaminants and their migration to the environment. Despite being classified as non toxic, the samples are not inert, which means that a specific site is required for their disposal instead of into the mine. Fluoride and sulfate are responsible for the chemical instability of the samples. Other elements, like Fe, Zn, Mn, U and Al, are present in significant concentrations. Uranium is present as an amorphous oxide. The main minerals of the samples, according to X-ray diffraction, are ettringite, gypsum and calcite (CaCO_3) and minor constituents are fluorite (CaF_2), gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and portlandite ($\text{Ca}(\text{OH})_2$).

Key words: uranium, acid mine, radioactive sludge, mine reclamation, environment contamination.

Introduction

The presence of high levels of contaminants in soils, tailings and wastes from mining activities has been extensively studied. Interest in the migration of these contaminants through geological media has increased because of the likelihood of surface and ground water contamination. The stability of chemical species in environmental materials is a critical factor during storage mostly because of degradation processes. Mining of uranium ore is one of the numerous examples of how anthropogenic activities can disturb the environment. From 1970 to 1996, a uranium ore processing mill operating at Poços de Caldas, Brazil generated tons of tailings and wastes that were disposed of near the mine. Sulfide oxidation caused acid mine drainage whose major contaminants are the radionuclides U and Th and toxic elements Mn, Zn and F. The humid climate of the region intensifies the acid mine drainage problem. The process that has been used for neutralization of the acid water produces a sludge that has been pumped back into the previous mine opening. The sludge contains high concentrations of uranium in the range 0.3% to 0.6%, higher than the ordinary uranium ores, and it is permanently in contact with the acid water that is produced at the mine. Therefore, the sludge stands out as a potential hazardous waste and may create a serious environmental problem since remobilization and migration of the toxic elements cannot be ignored. Here, the pH condition is the governing factor for metal-related problems. In addition, according to Fernandes et al. (1998), while neutralization of the water may be effective in reducing the concentrations of the contaminants to acceptable limits, it cannot be acceptable in terms of cost-effectiveness. The present work is part of a broader project aimed at providing knowledge for the selection of appropriated remediation strategies in view of the recent process of mine decommissioning. The objective of the current study is to present a chemical and mineralogical characterization as well as the classification of the sludge as hazardous or non-hazardous material according to leaching procedures. The determination of the main contaminants will provide a thorough understanding of the sludge's behavior as a support for future decisions.

Methods

Solid samples used in this investigation were identified as: fresh sludge (sampled at neutralization tank); intermediate sludge (disposed between 1 to 10 years) and aged sludge (disposed more than 10 years ago). Disposals of different ages were chosen in order to investigate if changes in environmental conditions can potentially affect metal availability and/or mobility. Samples were provided by Indústrias Nucleares do Brasil.

Characterization of the samples was carried out by combining X-ray diffraction analyses (Rigaku, Geigerflex model), atomic absorption analyses after the digestion of the solid sample and energy-dispersive X-ray spectrometry (Kevex system).

Leaching procedures were carried out with distilled water and acetic acid solution based on standard procedures (ABNT NBR10004/2004; NBR10005/2004). Trace elements were analyzed by atomic absorption spectroscopy and ICP-MS spectrometry.

Results and Discussion

Mineralogical and Chemical Characterization

Sample characterization is a very important stage of the research process since it provides a deep knowledge of the material which is crucial to answer questions, understand behaviors and propose solutions for the next steps. Table 1 presents the results obtained by Kevex analyses for U and Rare Earths. Uranium content is very pronounced in the three samples and is higher than in the majority of the current uranium ores, which means that it is also a significant source of this element. The Rare Earths content is also relevant, mainly in the intermediate sludge. More than 70% of the Rare Earths consist of the elements La and Ce.

Table 1 Percentage of Rare Earths and Uranium in the samples

Sample	Fresh (%)	Intermediate (%)	Aged (%)
Rare Earth	4.455	9.002	2.76
U (%)	0.24	0.68	0.58

The following Rare Earth elements were detected: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Sr, Y, Zr. Wet analyses showed that the sludges consist mostly of calcium and sulfate because of acid mine generation and precipitation treatment with lime. In addition, the elements Fe (0.5% to 7.7%), Mn (1.4% to 4.3%), Al (1.7% to 3.9%), Si (1% to 2.8%), F (0.7% to 2.5%), Mg (1% to 2.8%), and Zn (0.4% to 0.7%) were also identified. Besides uranium, manganese and zinc are the metals that cause most concern, mainly in the intermediate and aged materials. There is also a great concern about fluoride because it is a very toxic element and, according to Brazilian legislation, its presence may characterize the sludge as hazardous.

X-Ray diffraction was carried out with the samples as received and after gypsum solution using water. According to table 2, the predominant crystallized phases are ettringite and gypsum. After the solution of the gypsum in the intermediate sample, it was possible to identify some other crystallized phases that were not previously identified, such as calcite, fluorite, gibbsite and portlandite. In addition, it was verified that more than 70% of that sample consists of amorphous material. The identification of the crystallized phases was important here because the use of some properties of certain minerals to incorporate and store critical components in their crystal lattice has been reported in the literature. Forstner and Haase (1998) postulated that minerals which exhibit no hydraulic reaction, named “reservoir minerals” can form a widespread inert storage medium within a landfill, reducing water permeability and consequently the dispersion of pollutants. Ettringite and some Ca, Al and metal hydroxysalts are examples of reservoir minerals and can contribute to stabilization of pollutants. Ettringite, in particular, can act as a “storage mineral” for chloride and metal ions. Experimental studies carried out by these authors on the leachability of salts and metals incorporated in these kinds of materials indicate high rates of release for sulfate ions, but not for cadmium and zinc. As ettringite is one of the most prevalent minerals sampled in this study, it was expected that it could act as a reservoir for the metal constituents.

Table 2 Percentage of each crystallized phases identified.

Sample	Crystallized phases (>50%)	Crystallized phases (>30%)	Crystallized phases (<10%)	Crystallized phases (<5%)
Fresh sludge	Ettringite	-	Calcite	Bassanite /Gypsum
Intermediate sludge	Gypsum	Ettringite	-	Anidrite / Bassanite
Aged sludge	Ettringite	-	Wattevilleíte	Bassanite /Gypsum
Intermediate after gypsum removal	Amorphous material	-	Calcite/ Fluorite Gibbsite/Portlan dite	-

Anidrite: CaSO_4 ; Bassanite: $\text{CaSO}_4 \cdot \text{H}_2\text{O}_2$; Calcite: CaCO_3 ; Ettringite: $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$; Gypsum: $\text{CaSO}_4 \cdot \text{H}_2\text{O}$; Watevilleíte: $\text{Na}_2\text{Ca}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$; Calcita (CaCO_3); Fluorite (CaF_2); Gibbsita ($\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$); Portlandita $\text{Ca}(\text{OH})_2$

Classification

The ABNT NBR 10004/2005 standard procedure was used to classify the samples as toxic or non-toxic. The samples were put in contact with acetic acid solution for a pre-determined time, then the liquid phase was analyzed for specific elements and compared to the standard limits. It should be noted from Table 3 that soluble concentrations of all metal ions would not exceed the upper threshold permitted limit and the samples would be classified as non-toxic.

Table 3 Leaching with acetic acid according to ABNT NBR 10004/2005.

Elements	Permitted Limit (mg.L ⁻¹)	Fresh (mg.L ⁻¹)	Intermediate (mg.L ⁻¹)	Aged (mg.L ⁻¹)
As	1.0	< 0.09*	1.88*	< 0.09*
Ba	70.0	< 10	< 10	< 10
Cd	0.5	< 0.5	< 0.5	< 0.5
Pb	1.0	< 1.0	< 1.0	< 1.0
Cr	5.0	< 0.20	< 0.20	< 0.20
F ⁻	150.0	6.60	7.40	7.40
Hg	0.1	< 0.10*	< 0.10*	< 0.10*
Ag	5.0	< 1.0	< 1.0	< 1.0
Se	1.0	< 0.70*	1.71*	< 0.70*
Cu	**	< 0.01	< 0.01	< 0.01
Fe	**	< 0.01	< 0.01	< 0.01
Al	**	3.60	2.35	3.13
Zn	**	16.0	8.0	8.0
Mn	**	0.054	< 0.01	< 0.01
Ca	**	800	660	750
SO ₄ ⁻²	**	1.000	1.000	1.000
U	**	<1	<1	<1

* Values in $\mu\text{g.L}^{-1}$; ** Values not determined by Brazilian Legislation ABNT NBR 10004:2004

Although the samples were classified as non-toxic, they should be classified as inert or non inert. The ABNT NBR 10005/2005 procedure comprises placing the samples in contact with water and analyzing the supernatant for the elements listed in table 4. According to these data, all samples exceeded the permitted limit for fluoride and sulfate. With regard to the other elements, no threshold values have been exceeded, which is explained by the high final pH (around 8) of the leachate, which

favors the precipitation of the majority of the contaminants. On the other hand, according to Ladeira and Ciminelli 2004, both low and high pH values will have unfavorable effects on the mobility of heavy metals. Therefore, the sludges were classified as non-inert and could not be deposited on landfills without major precautionary measures. This means that the current site used for the sludge disposal at Poços de Caldas is improper and should be avoided. Migration of the contaminants to the environment should not be disregarded.

Table 4 Classification of the samples as inert or non-inert.

Elements	Permitted Limit (mg.L ⁻¹)	Fresh (mg.L ⁻¹)	Intermediate (mg.L ⁻¹)	Aged (mg.L ⁻¹)
Al	0.2	< 0.2	< 0.2	< 0.2
As	0.01	< 0.09*	< 0.09*	< 0.09*
Ba	0.7	14.2*	10.4*	20.8*
Cd	0.005	0.24*	0.01*	0.16*
Pb	0.01	1.5*	0.38*	0.57*
Cu	2.0	< 0.5	< 0.5	< 0.5
Fe	0.3	< 0.3	< 0.3	< 0.3
F ⁻¹	1.5	5.60	7.00	4.30
Mn	0.1	< 0.1	< 0.1	< 0.1
Hg	0.001	< 0.1*	< 0.1*	< 0.1*
Ag	0.05	0.20*	< 0.09*	< 0.09*
Se	0.01	< 0.7*	< 0.7*	< 0.7*
SO ₄ ²⁻	250	1.692	1.589	1.873
Zn	5.0	< 0.2	< 0.2	< 0.2
U	**	< 1	< 1	< 1

* Values in µg.L⁻¹; ** Values not determined by Brazilian Legislation ABNT NBR 10005:2004

Results from sequential extraction procedures (data not shown) indicated that the metals are associated mainly with amorphous materials and not with crystallized phases, e.g. ettringite as was expected. Only 10% of the metals are associated with crystallized phases.

Conclusions

Sample characterization showed that the samples consist mainly of U, Rare Earths, Fe, Mn, Zn, Ca and sulfate. The predominant crystallized phases are ettringite and gypsum, the formation of which results from the precipitation process. The sludges are considered non-toxic material, but not inert, which means that they should not be deposited on landfills without major precautions. For that reason, the decommissioning process may take into account the chemical instability of the sludge and the great possibility of migration of contaminants to the surroundings.

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References

- A.C.Q. Ladeira, V.S.T. Ciminelli (2004), Adsorption and desorption of arsenate on an oxisol and its constituents. *Water. Res.* 38: 2087-294.
- H.M. Fernandes, M.R. Franklin, L.H. Veiga (1998), Acid rock drainage and radiological environmental impacts. A study case of the Uranium mining and milling facilities at Poços de Caldas, *Waste Management* 18: 169-181.
- U. Forstner, I. Haase (1998) Geochemical demobilization of metallic pollutants in solid waste –implications for arsenic in waterworks sludges. *J. Geo. Exploration* 62: 29-36.
- Standard Procedure: Associação Brasileira de Normas Técnicas: ABNT NBR10004/2004; NBR10005/2004. Resíduos Sólidos- Classificação, ABNT, Brasil.