LEACHING OF URANIUM FROM THE OSAMU UTSUMI MINE WASTES, INB CALDAS, MINAS GERAIS

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ABSTRACT

Mining is one of the leading sectors of the Brazilian economy and as any other anthropogenic activity it generates residues that impact the environment directly. The Osamu Utsumi Mine, which belongs to the Nuclear Industries of Brazil (INB), operated from 1982 to 1995 with the activities of mining and metallurgical treatment of the uranium ore. Since then the INB has as a main environmental problem, the generation of acid mine drainage from wastes having its pH around 3. The chemical treatment of this acid water incurs an extremely high cost and generates a precipitate that is rich in some metals, including uranium. This precipitate has been disposed of in the mine opening and has caused an overload of chemical pollutants and radioactive elements in a place that was not planned to receive this volume of residues and does not meet the necessary condition for the construction of a repository. The content of uranium in the precipitate is approximately 0.25% - similar to the content of the metal found in the ore in the Caetité Mine (BA) - around 0.29%. The recovery of this uranium from the precipitate would generate a total of 150 tons of $\text{U}_3\text{O}_8$. In the present study an alkaline leaching process was carried out aiming at recovering the uranium from sludge samples disposed of for over 20 years. Sodium carbonate and bicarbonate were used as the leaching agents. The experiments were carried out by varying the concentrations of the leaching agents, extraction time and the solid percentage. The other parameters such as temperature, particle size and agitation were kept constant. The results showed that the recovery of the uranium can reach 100% in 24 hours. The uranium concentration in the solutions is around 250 mg.L$^{-1}$ when using 10% of solids. Preliminary results showed that the recovery of uranium from the sludge would be a feasible practice. The conversion of an environmental liability into a valuable product is one of the most important objectives of this work.

Key words: uranium, acid water, carbonate leaching, sludge

1 INTRODUCTION

Mining and milling of uranium ore has the potential to cause environmental pollution in nearby water courses and aquifers with radionuclides, metals and other contaminants. The Osamu Utsumi Mine belonging to Indústrias Nucleares do Brasil, INB, located in Caldas/MG extracted and processed uranium from 1982 to 1995. The operations contributed to the formation of two principal sources of environment contaminants: waste rock dump and tailings dam. After 13 years the uranium mining and milling operations have ceased. Since then, the mine has an active maintenance system whose focus is the treatment of the acid drainage generated in the open pit of the mine, waste dumps and tailings dam. Acid mine drainage (AMD) is a serious problem in the mining and mineral industry. AMD is especially harmful because it can occur indefinitely - long after mining has ended. It is also relevant due to the environmental impact and the high costs involved in its neutralization [1].
AMD originated in the Osamu Utsumi mine occurs owing to the oxidation of the great amount of sulfide waste and tailings with low uranium content (250mg/kg) disposed of in the mine’s surrounding areas in the presence of water and oxygen. In the oxidation process sulfuric acid formation occurs alongside the consequent reduction of the pH of the draining water. Once acid drainage is originated, the metals are discharged into the surrounding environment and become readily available to biological organisms. The occurrence of pyrite, FeS$_2$, as a constituent of the ore plays an important role in the generation of acid drainage and the main reaction of the oxidation may be written according to equation 1\[2, 3\].

$$\text{FeS}_2(s) + 7/2\text{O}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{Fe}^{2+}(aq) + 2\text{SO}_4^{2-}(aq) + 2\text{H}^+ (aq)$$ (1)

Acid mine waters typically contain high concentrations of both dissolved heavy metals and sulphate, turbidity and pH values as low as 2 \[4\]. These conditions may prohibit the discharge of untreated acid mine waters into public streams since they have a detrimental effect on aquatic plant and fish life. The chemical treatment of the AMD generated in the INB Caldas is carried out through the increasing of its pH, initially around 3, up to values next to 10, with the addition of lime - Ca(OH)$_2$. The objective of this process is the simultaneous precipitation of metallic ions as hydroxides and the increase in pH. \[1, 5, 6\]. The sludge produced has been disposed of into the open pit over 20 years due to the exhaustion of the capacity of the tailing dam. This practice has been a serious problem for the general management strategy in the facility and can pose a threat to the environment.

The uranium content in the precipitate generated in the treatment of the AMD in Caldas is around 0.25%, and is similar to the content found in other ordinary uranium ores that have been treated throughout the world \[7\]. The precipitate, also called alkaline sludge, consists in a significant source of uranium. The recovery of the uranium would generate a total amount of 150 tons of U$_3$O$_8$. The extraction of the uranium from this sludge can be achieved through leaching techniques, such as alkaline leaching using carbonate and bicarbonate of sodium as leaching agents \[8\].

Uranium is characteristically leached from uranium ores by acid extractants or carbonate based extractants. The extraction of uranium ores with sulfuric acid will be cheaper than the process developed with nitric acid. Although the leaching using sulfuric acid is cited as one of the most common processes for the recovery of uranium ores, sodium carbonate has also been used in the mining industry to extract uranium from carbonate bearing ore. The major disadvantage of the carbonate leaching process is the slow dissolution kinetics associated with the alkaline process, as compared with acid leaching \[8, 9, 10\]. Several benefits of the carbonate leaching process include high selectivity (because many metals are not soluble in alkaline solutions) and high purity of the solution produced, which makes direct precipitation of uranium from the leach liquor easier \[8\]. The removal of uranium from an alkaline medium is possible due to the formation of uranyl tricarbonate, [UO$_2$(CO$_3$)$_3$]$^4^-$ a very stable anion in the pH range 8-11 \[9, 11\]. The efficiency of the carbonate-bicarbonate extractions depend on the mineralogical characteristics of the ore. Materials containing uranium in the tetravalent state require oxidant agents (e.g. sodium perchlorate, potassium permanganate and hydrogen peroxide) in order to convert it into uranium hexavalent, which it is the most soluble form of the metal. In addition,
carbonate leaching is particularly advantageous in the treatment of ores with a high content of carbonates, since these minerals are not attacked by carbonate solutions.

The goal of this research is to examine the applicability of hydrometallurgical techniques such as alkaline leaching for the extraction of the uranium present in the precipitate found in the INB Caldas through the determination of the effects of various parameters, like carbonate and bicarbonate concentration and oxidant reagents in the final recovery.

2 EXPERIMENTAL PROCEDURES

2.1 Sample preparation
The sludge sample was collected in the open pit of the Osamu Utsumi mine. The sample was dried in air at 50°C for 24 hours, and ground to an average particle size of 0.21 mm.

2.2 Chemical and mineralogical characterization
The Uranium was analyzed in an energy-dispersive X-ray spectrometer (Kevex system, model SIGMAX-9050). This technique uses an americium source, $^{241}$Am, for $\gamma$-ray generation and allows the detection of uranium in a high sensitivity level (10 $\mu$g.g$^{-1}$), [7]. The identification of the crystalline phases was determined by X-ray diffraction (XDR), powder method. The X-ray diffraction equipment (Geigerflex model) has a half-automatic Rigaku X-ray diffractometer and copper pipe X-ray.

2.3 Uranium leaching tests
Leaching experiments were carried out in batches and the influence of the following variables was investigated: concentration of the reagents, reaction time (2, 4, 6 and 24 hours) and solid percentage (10, 20 and 40%). The solution concentrations were 0.25, 0.40, 0.70 and 1.00 mol/L of sodium bicarbonate and 0.25; 0.50; 0.75 and 1.75 mol/L of sodium carbonate solutions, respectively.

Specific amounts of the sample were exposed to different concentrations of sodium bicarbonate and sodium carbonate solutions for pre-determined periods. All batch experiments were carried out in beakers under mechanical agitation. At the end of the experiments the solid/liquid separation was accomplished by centrifugation. For centrifugation, 15 mL of the slurry was transferred to polycarbonate centrifuge tubes of 50 mL and centrifuged at 4000 rpm for 15 min. The liquid phase was analyzed for $\text{U}_3\text{O}_8$ by means of the kevex system.
3 RESULTS AND DISCUSSION

3.1 Characterization of the sludge

X-ray diffraction (XRD) analysis showed ettringite as the predominant phase (> 60% of occurrence), gypsum, CaSO₄.2H₂O, as the major phase (< 30% occurrence), calcite (CaCO₃) with occurrence smaller than 10% and the bassanite, CaSO₄.0.5H₂O as a minor phase < 5%.

All minerals identified above present calcium in its constitution, resulting from the neutralization of the acid water with lime, Ca(OH)₂. The neutralization leads to the concomitant precipitation of ions such as iron, aluminum, sulphate and other metals present in the acid effluent. The ettringite, \( \text{Ca}_6\text{Al}_2(\text{SO}_4)_3.(\text{OH})_{12}.26\text{H}_2\text{O} \), was the predominant phase due to the favorable chemical condition of the system. The pH range - 10.7 to 12.5 alongside the high concentration of the ions in the solution enhance the formation of ettringite. Gypsum and bassanite confers to the sample some undesirable characteristics such as high plasticity and viscosity, which hinder the leaching process of the uranium since the slurry hardens rapidly. Another problem is the consumption of carbonate ions in the leaching solution by calcium ions, originating from the dissolution of minerals, producing calcite or calcium carbonate, CaCO₃.

The chemical characterization of the sludge showed: 30.3% CaO, 10.9% Al₂O₃, 18.8% SO₄²⁻, 2.9% rare earths (La₂O₃, CeO₂, Nd₂O₃, Y₂O₃ and SrO), 0.92% Fe₂O₃, 0.25% U₃O₈, 56.7 ppm ThO₂ and 4.29 ppm of Ra. Sulphur occurs due to the oxidation of pyrite and the generation of sulfuric acid, therefore being precipitated as gypsum in alkaline pH. The presence of other elements is the result of the dissolution of the rocks in the acid environment.

3.2 Alkaline leaching

The pH of the sludge was determined in water (1:1) and the average pH value found was 9 [12]. This pH favors the application of the alkaline leaching technique since it avoids excessive consumption of reagents in order to lower the pH required in the execution of the acid leaching.

3.2.1 Effect of the carbonate concentration

In order to study the influence of carbonate, the concentration of the bicarbonate was kept constant at 0.25 mol/L according to previous studies reported in literature [8, 13].

Samples of ground sludge (16.67 grams each) were mixed with 150 mL sodium bicarbonate solutions containing 0.25, 0.50, 0.75, 1.75 and 1.75 mol/L sodium carbonate for 1, 2, 3, 4, 5, 6 and 24 hours. The results showed that the highest leaching extraction achieved was about 43% using \([\text{CO}_3^{2-}] = 0.50 \text{ mol/L} \) (Fig. 1).
In the leaching process the role of carbonate ions is to make uranium available in the solution through the formation of the soluble uranyl tricarbonate anion, as shown in the reaction 2:

$$\text{UO}_3^{(aq)} + 3\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightarrow [\text{UO}_2(\text{CO}_3)_3]^4- (aq) + 2\text{OH}^- (aq)$$  \hspace{1cm} (2)

An increase in the carbonate concentration tends to precipitate part of the dissolved uranium through a reaction with the hydroxyl ion, thus forming sodium diuranate and, consequently, decreasing the amount of the metal in the solution.

In conclusion, as the best result obtained was with $[\text{CO}_3^{2-}] = 0.50 \text{ mol/L}$ all the subsequent experiments were carried out with this concentration.

### 3.2.2 Effect of the bicarbonate concentration

The influence of the sodium bicarbonate at a carbonate concentration set to 0.50 mol/L is represented in Fig. 2. A general improvement in the leaching extraction was observed as the
bicarbonate content increased. The pH of the system was between 9.4 and 11, depending on the bicarbonate concentration.

![Figure 2](image)

**Figure 2 – Effect of the bicarbonate concentration at a constant carbonate concentration in the uranium extraction.** $[\text{CO}_3^{2-}] = 0.50 \text{ mol/L}; T = 25^\circ \text{C}$, and 10% solids.

The dissolution of the uranium was favored in $[\text{HCO}_3^-] = 1.00 \text{ mol/L}$ where it was possible to get extractions above 95% in a 24 hour leaching time. Under this condition, the final solution in the leaching process had a concentration of approximately 0.25g/L of $\text{U}_3\text{O}_8$. Therefore, the bicarbonate concentration in the subsequent tests was kept constant at 1.00 mol/L.

Bicarbonate is added to the leaching solutions to avoid re-precipitation of the hexavalent uranium, for it prevents the reaction between the hydroxyl ion and the uranium from the formation of the insoluble uranates, in this case $\text{Na}_2\text{U}_2\text{O}_7$ as presented in equation 3 and 4 [8].

$$\text{HCO}_3^-(aq) + \text{OH}^-(aq) \rightarrow \text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l)$$  

$$2[\text{UO}_2(\text{CO}_3)_3]^+(aq) + 6\text{OH}^-(aq) + 2\text{Na}^+(aq) \rightarrow \text{Na}_2\text{U}_2\text{O}_7(s) + 6\text{CO}_3^{2-}(aq) + 3\text{H}_2\text{O}(l)$$  

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3.2.3 Effect of the oxidant reagents

Uranium may occur in nature in the reduced (tetravalent) state, oxidized (hexavalent) state or may be present in a combination of the two. The uraninite, the main uranium ore of Poços de Caldas, is one example. Uraninite contains uranium as an oxide which formula is represented as UO$_2$, but in fact it has a composition between UO$_2$ and UO$_3$. Uranium is most stable in the tetravalent form, therefore the metal is principally found in nature in that oxidation state. Uranium present in the mineral as tetravalent must be oxidized to the hexavalent state before dissolution occurs. Many oxidants agents are utilized, e.g. air, NaClO$_3$, H$_2$SO$_5$, O$_3$, pyrolusite and H$_2$O$_2$ [5, 8, 14]. Hydrogen peroxide 45% p/p was used in the present study to investigate the effect of oxidation on the uranium leaching process [9, 10, 13, 15]. Large excess of hydrogen peroxide, 10 times the stoichiometric amount, was used in order to assure that all the uranium would be oxidized. Fig. 3 represents the effect of oxidant agent on the extraction of uranium.

When hydrogen peroxide (H$_2$O$_2$) was added to the slurry, no increase in the removal of uranium was detected in any of the conditions studied. This was justified by the natural oxidation of the tetravalent uranium as a product of the acid mine water generation. The phenomenon occurs when the sulfide ores, such as FeS$_2$, are exposed to the weather leading to the formation of Fe$^{3+}$.
which, in turn, oxidizes the uranium and makes it available in its hexavalent form. Ferric ion is well known and documented as an effective oxidant for uranium. Therefore, it is useless to use oxidant agents during the metal leaching, as all the uranium is believed to precipitate as U⁴⁺.

3.2.4 Effect of the slurry density

The effect of the slurry density on the leaching of uranium at 25°C, \([\text{CO}_3^{2-}] = 0.50\ \text{mol/L}\) is show in Table 1.

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<tr>
<th>Bicarbonate concentration (mol/L)</th>
<th>Slurry Density</th>
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<tbody>
<tr>
<td></td>
<td>10%</td>
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<tr>
<td>0.70</td>
<td>100</td>
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<td>1.00</td>
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As expected, the leaching of uranium decreased with the increment of the percentage of solid. Part of this behavior is due to the presence of minerals, such as the gypsum, which confers plasticity and viscosity to the system. Either excessive viscosity or plasticity has a deleterious effect on the rate of the leaching and on the availability of the metal in solution. At elevated slurry densities, e.g. above 20 percent solid, the maximum quantity of uranium extracted was 2.9%, which is considered irrelevant to the process. The highest amounts of uranium extracted in the experiments were at 10 and 20 percent solid. At 10 percent solid, the uranium extractions were 100% for all tests, independent of the concentration of the bicarbonate in the leaching solution. At 20 percent solid, the maximum extraction was approximately 76.5% for 1.00 mol/L of sodium bicarbonate. These results showed that the concentration of the bicarbonate seems to be independent of the slurry density in the uranium extraction. However, high concentrations of bicarbonate tend to be more effective when working with 20 percent solid due, mainly, to the increase in the ionic strength of the solution and the moderate interference of viscosity. The optimum working condition should be 10 percent solid which produces a liquor containing 250mg/l of uranium.

4 CONCLUSIONS

The data obtained in this work demonstrates that the use of sodium carbonate/bicarbonate in the leaching process leads to an extraction of up to 100% of the uranium from the sludge sample of Poços de Caldas. The best conditions that should be used to attain extractions higher than 95%
of the metal were: 10% percent solid, \([\text{HCO}_3^-] = 1.00 \text{ mol/L}, [\text{CO}_3^{2-}] = 0.50 \text{ mol/L}\) and a 24 hour leaching time. The uranium concentration in the leached is around 250 mg/L. The following step is the recovery of the uranium from the liquor through its precipitation as yellow cake \(\text{U}_3\text{O}_8\).

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REFERENCES

7. GOMIERO L.A.; SCASSIOTTI, W.F.; MORAIS, C. A. “Dynamic leaching of uranium ore from Caetité s facilities BA, Brazil a comparison with the heap leaching process”. In: VII Meeting of the Southern Hemisphere on Mineral Technology XXII Encontro Nac. de Tratamento de Minérios e Metalurgia Extrativa, Ouro Preto. Universidade Federal de Ouro Preto, pp.51-57 (2007).

