ACID LEACHING OF URANIUM PRESENT IN A RESIDUE FROM MINING INDUSTRY

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ABSTRACT

The acid mine drainage is one of the most important environmental problems associated with mining of ores containing sulfides. The treatment of these acid effluents, which contains high concentrations of dissolved metals and anions, is generally by liming. The wastes generated in the liming process may present significant toxicity and their storage in inappropriate places waiting for treatment is a common issue that requires solution. Osamu Utsumi Mine located in the city of Caldas, Minas Gerais, has been facing this problem. The residue of this mine consists of an alkaline sludge generated from the neutralization of the pH of acid mine drainage and is rich in various metals, including uranium. The main concern is the long term stability of this residue, which is in permanent contact with the acid water in the open pit. The recovery of uranium by hydrometallurgical techniques, such as acid leaching, can be a viable alternative on the reuse of this material. This study aimed at establishing a specific leaching process for the recovery of uranium present in the sludge from Caldas uranium mine. Some parameters such as solid/liquid ratio (0.09 to 0.17), time of leaching (1 to 24 hours) and concentration of sulfuric acid (pH from 0 to 3.0) were assessed. The results showed that it is possible to extract 100% of uranium present in the sludge. The concentration of U_3O_8 in the residue was 0.25%, similar to the content of the vein ores which is around 0.20% to 1.0%. The best experimental leaching condition is solid/liquid ratio of 0.17, pH 1.0 and 2 hours of reaction at room temperature (25 ° C). The content of uranium in the liquor is around 440 mgL^{-1}. The recovery of the uranium from the liquor is under investigation by ionic exchange.
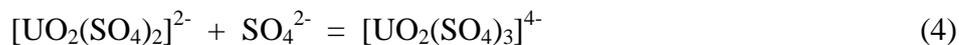
1. INTRODUCTION

The chemical element uranium is found over the earth's crust as a constituent of most rocks. It is main commercial application is as fuel for nuclear reactors to generate electricity [1]. It is also used in the production of radioactive material for use in medicine and food production. Uranium is found in nature mainly as oxide. Despite of large amount of oxides formed by the uranium, only two are most important: UO_2 and U_3O_8 since they constitute most of the uranium ores [2]. The ore reserves, to be economically viable, depend on the content of uranium as well as the technology used to recover the metal.

Leaching is the process of extracting an element present in minerals, industrial wastes or metal concentrates through its dissolution in a liquid phase. It can be performed in acidic, basic or neutral solution. In the leaching process it is common the use of salts, complexing agents, oxidizing and reducing agents. The leaching of uranium is dependent, in part, of the

physical characteristics of ore, type of mineralization, ease of release, and nature of the mineral constituents. The basic principles established for the leaching of uranium are [3]: i) concentration of leaching agent; in the case of this study the concentration of H_2SO_4; ii) temperature; usually the leaching rate increases by a factor between 1.5 and 2.0 to 10 ° C increase in temperature; iii) grain size of the ore; interferes with the degree of metal release and the smaller the grain size the greater the release of the metal.

Uranium can be found in nature, especially in oxidation states U^{4+} ou U^{6+}, mostly in the form of carbonates, sulfates, phosphates, among other complex oxides. In its reduced form, U^{4+}, uranium practically does not dissolve, but when it is oxidized to U^{6+}, it becomes easily leachable at room temperature [3], thus increasing the yield of recovery.

During the acid leaching, sulfuric acid can ionize in solution forming sulfate, bisulfate and hydrogen ions. The reaction these species with the hexavalent uranium, which dissolves as the UO_2^{2+} cation, produces the uranyl sulfate complexes as described by the reactions below [3]:

$$UO_3 + 2H^+ = UO_2^{2+} + H_2O \qquad (1)$$

$$UO_2^{2+} + SO_4^{2-} = UO_2SO_4 \qquad (2)$$

$$UO_2SO_4 + SO_4^{2-} = [UO_2(SO_4)_3]^{2-} \qquad (3)$$

$$[UO_2(SO_4)_2]^{2-} + SO_4^{2-} = [UO_2(SO_4)_3]^{4-} \qquad (4)$$

Uranium can occur in any of the soluble forms above, depending on the concentrations of uranium and acid, temperature and other variables in the system. For the recovery of uranium from the leach liquor, the production of uranyl sulfate anionic complexes, like $[UO_2(SO_4)_3]^{2-}$ and $[UO_2(SO_4)_3]^{4-}$, is an important advantage of using sulfuric acid, since the anionic resins are more selective for uranium species.

The present work focuses on one of the biggest problems of mining that are the wastes generated by this activity. The waste is stored in the Osamu Utsumi mine, Caldas Municipality, Minas Gerais. It consists of an alkaline sludge generated from the neutralization of the pH of acid mine drainage and is rich in various metals, among which is uranium. The recovery of uranium by hydrometallurgical techniques, in this case acid leaching can be a viable alternative on the reuse of this material once it has been disposed into the mine opening and contains about 0,25% of U_3O_8.[4]

2. MATERIALS AND METHODS
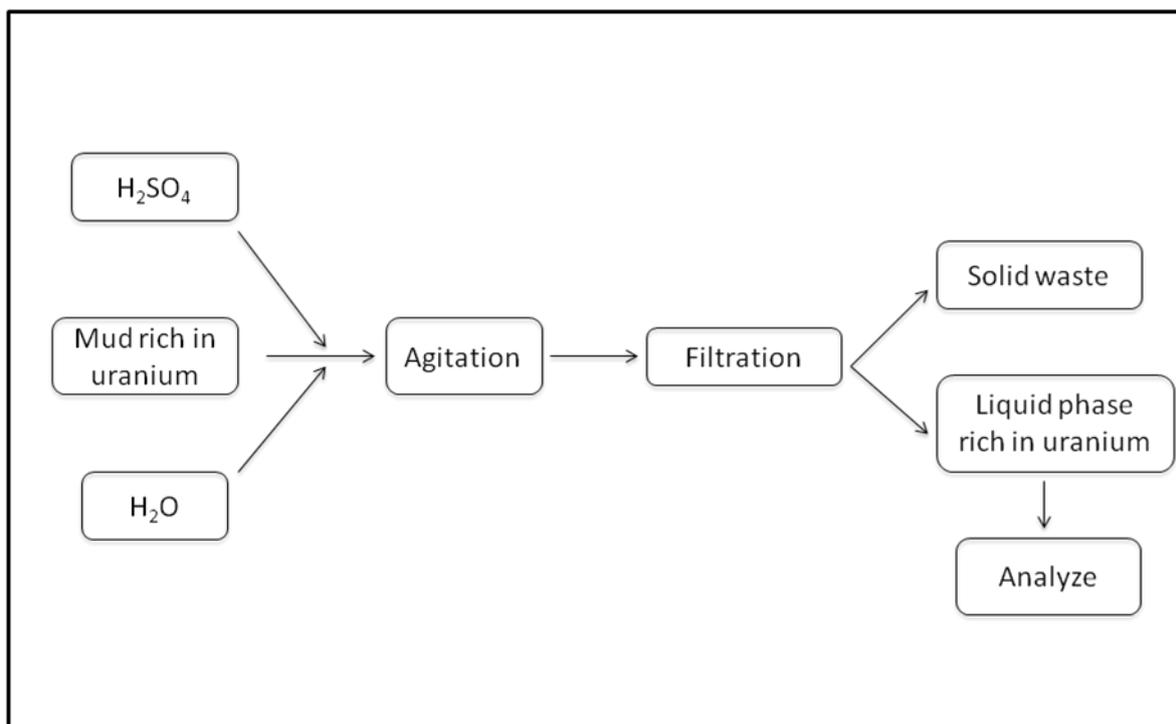
Figure 1. Acid leaching flowchart.

Figure 1 shows the flow chart of the leaching tests. Initially, it is placed in one beaker a specific volume of water and sulfuric acid, and a predetermined mass of the dry residue containing the uranium. Then the slurry is mechanically agitated for a certain time. In the end, the slurry was filter and then the liquor, rich in uranium, is separated from the solid waste which is low in uranium content. The solid waste is washed with distilled water and the liquor is sent to uranium determination.

2.1. Sample

The sample came from the neutralization of acid mine drainage generated in Caldas mine and was collected in the mine opening. It was dried at a temperature of 50 ° C for a period of 24 hours in an oven brand QUIMIS with forced air. Subsequently, it was milled in a ball mill for 30 minutes, sieved through a sieve of 0.21 mm and homogenized in order to produce samples of about 50g each, which were packed in plastic bags properly identified.

2.2. Chemical and mineralogical characterization of the sludge

X-ray diffraction analyses (powder method) were carried out for mineralogical characterization, using a semiautomatic Rigaku diffractometer (Geigerflex Model) and CuK alpha monochromatic radiation. The working conditions were: power and operation amperage of 40 kW and 30 mA, step intervals at 0.5 s, and scale factor of 4 x 10^3 samples were run at a speed of 4°2θ mim^{-1}. The Mineralogical semi quantification of the crystalline phases was estimated by comparing the X-ray diffraction with the data of the ICDD (International Center Diffraction Data)/JCPDS (Joint Committee on Powder Diffraction Standard). Chemical

characterization was carried out though X-ray fluorescence techniques: (i) Kevex-Ray- (Model Sigmax- 9050) which consists of an X-ray source of [241]Am and Si(Li) detector and (ii) energy dispersive X-ray technique using Shimadzu model EDX-720.

2.3. Acid leaching procedure

Leaching experiments were carried out in batches and the influence of the following variables was investigated: concentration of the reagents, reaction time and solid/liquid ratio (0.09 and 0.17). The solution pHs were 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0.

Specific amounts of the sample were exposed to different pH concentrations for pre-determined periods. All batch experiments were carried out in beakers under mechanical agitation. During the leaching, aliquots of 25 mL of slurry were collected at specific periods. At the end of the experiments the solid/liquid separation was accomplished by centrifugation. For centrifugation, 25 mL of the slurry was transferred to polycarbonate centrifuge tubes of 50 mL and centrifuged at 4000 rpm for 15 minutes. The liquid and solid phase was analyzed for U_3O_8 by means of the Kevex system.

3. RESULTS AND DISCUSSION

3.1. Chemical and mineralogical characterization

The results from chemical analysis using fluorescence spectrometry X-ray (EDX) are presented in Table 1. The sample has high levels of calcium, aluminum, manganese and rare earths. It is observed that the concentration of U3O8 is 0.23%. Santos and Ladeira (2011) pointed out that this content is similar to the content of some ores processed in Brazil nowadays, whose values are very close to 0.30%.

Table 1. Characterization of the sample

Elements	Content (%)
U_3O_8	0.23
$CaSO_4$	37.70
$CaCO_3$	13.00
Al_2O_3	9.45
MnO	2.49
Rare earths	2.20
SiO_2	1.50
P_2O_5	0.73
Fe_2O_3	0.64

ZnO	0.26
SrO	0.027

The high content of calcium is mainly due to use of hydrated lime ($Ca(OH)_2$) as a reagent for the neutralization of the acid effluent. On the other hand, the sulfur, found in the form of sulfate, is due to oxidation of sulfides which produces the acid drainage. It was also verified the presence of other contaminants in the sample, for example, zinc and manganese.

3.2. Acid leaching

The choice for the use of acid leaching was based on previous studies on the alkaline leaching. The presence of carbonate ion in the liquor made difficult the recovery of uranium by ion exchange as the carbonate ions compete with the uranium complex for the resins sites. The sulfuric acid leaching then comes as an alternative. The formation of the uranyl sulfate complexes has an important advantage since the anionic resins are more selective for these kinds of complexes.

3.3. Effects of solid/liquid ratio

To assess the influence of solid/liquid ratio in the leaching, experiments were carried out at 0.09 and 0.17 solid/liquid ratio using solutions with different pH values. The leaching time was determined at 6 hours which proved to be enough for testing.

In general, there is a decrease in the extraction of uranium as the concentration of solids in the slurry increases. This can be explained by the presence of minerals such as gypsum, bassanita and ettringite that cause an increase in the plasticity and viscosity of the system. According to Santos and Ladeira (2011), the excess of viscosity and the plasticity act negatively in the leaching process, as the contact between the extraction solution and the solid surface is reduced.

The results presented in Figure 2 show the possibility of obtaining uranium extraction greater than 95%, using 0.09 to 0.17 solid/liquid ratio and pH near 1.0. For pH values higher than 1, yields were below 87%.
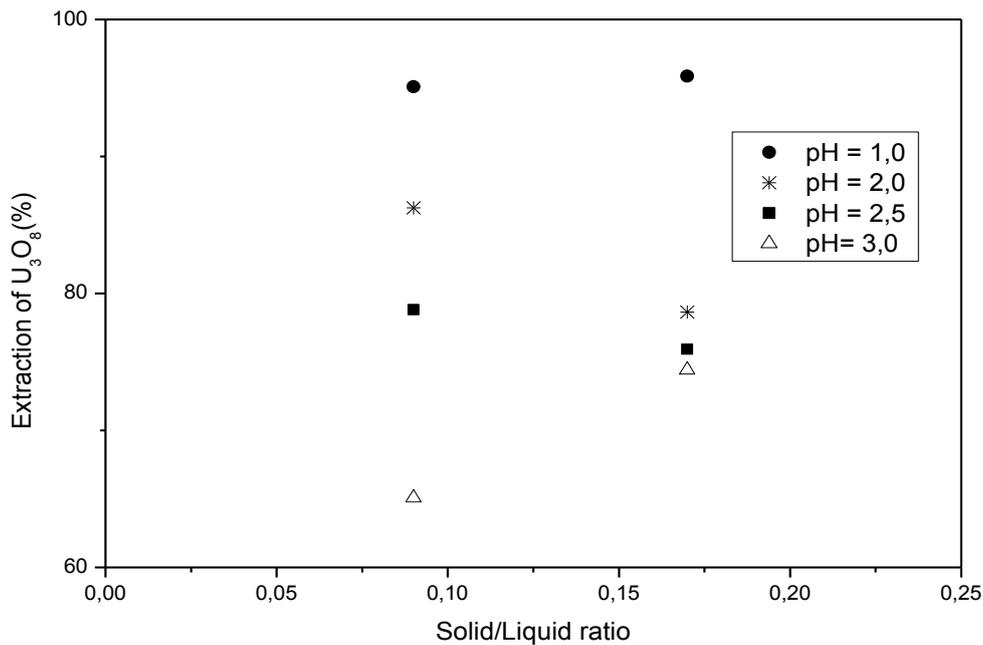
Figure 2. Effect of solid/liquid ratio and the pH concentrations on the extraction of uranium in room temperature and 6 hours leaching.

In spite of the same results obtained with 0.09 and 0.17 solid/liquid ratio, it was determined that the best condition for uranium extraction would be 0.17 solid/liquid ratio since this condition leads to near 100% extraction as well as process a larger amount of residue.

3.4. Effects of leaching time

In order to assess the kinetics of leaching and determine the optimal leaching time, aliquots were obtained at different time up to 24 hours. Figure 3 shows the data for these experiments.
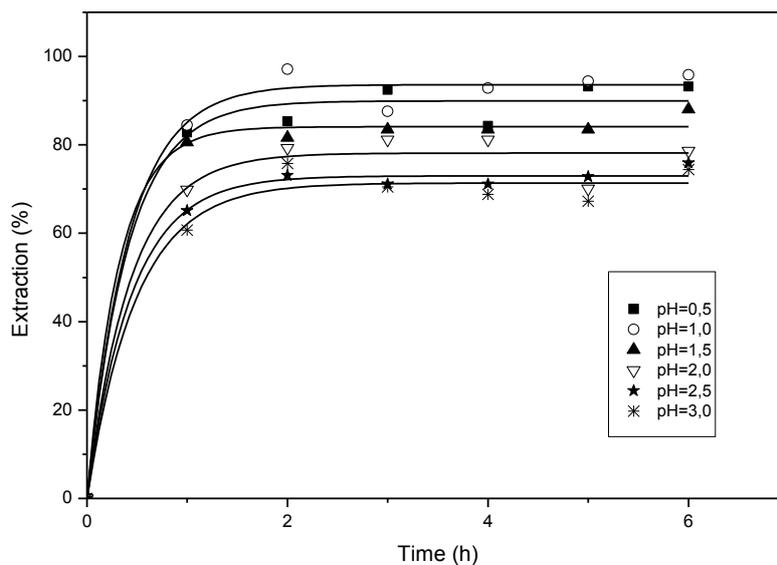
It was observed that the maximum extractions for all the pH values assessed were reached above 2.5 hours of leaching time, confirmed by the formation of the plateau in the curves presented.

The best results were achieved for the experiments at pH 0.4 and 1.0 because they present extractions higher than 90%. It was also observed that the experiment at pH 3.0 shows an extraction well below the others; that is approximately 60%.
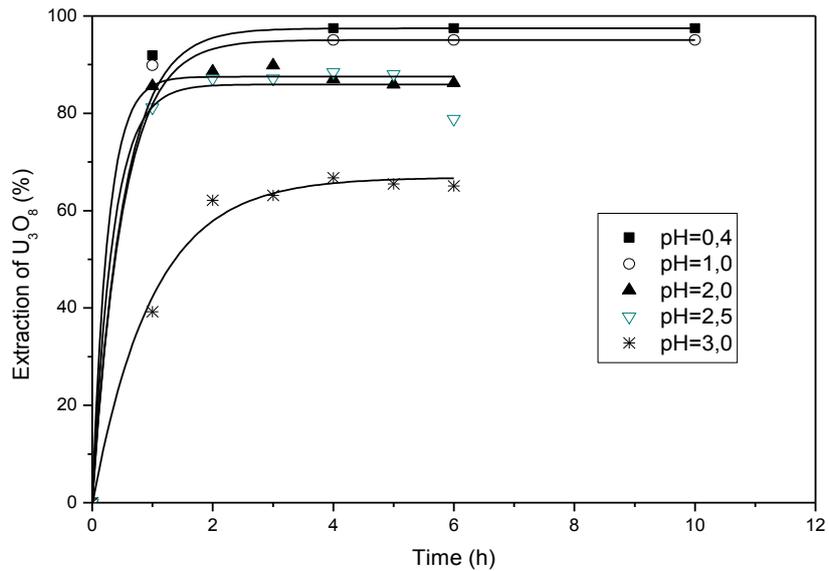
Figure 3. Effects of time in the uranium extraction; 0.09 solid/liquid ratio and room temperature.

Figure 4 presents the data for extraction at 0.17 solid/liquid ratio. It is observed that that only 2.0 hours of leaching test the , of extraction reaches its maximum for all experimental conditions assessed. However, the maximum extractions have different values between 65% and 98% according to the pH of the experiment.
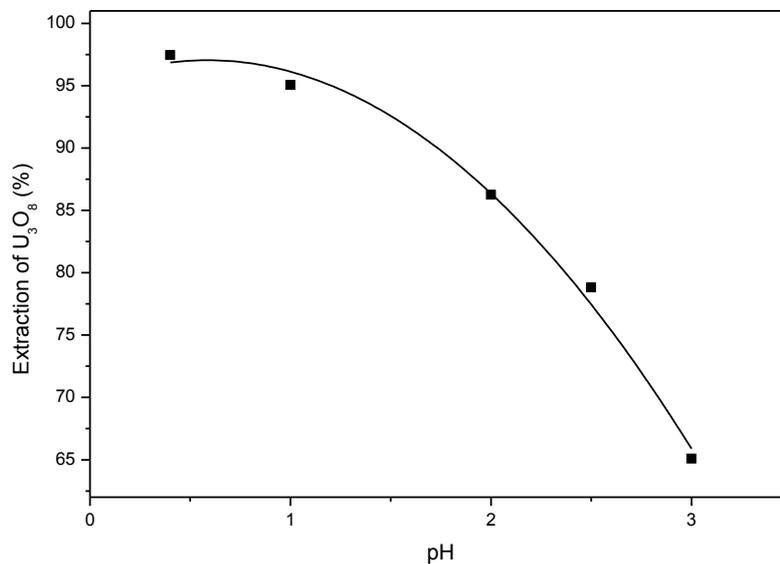

Figure 4. Effects of time in the uranium extraction; 0.17 solid/liquid ratio and room temperature.

It was observed that at pH = 1 the best yield for uranium the extraction was obtained, while for tests with 0.09 solid/liquid ratio the best performance occurs at pH below 1. In general, it was noted that the extraction occurs in a few hours of testing and the increase in pH imply in a decrease in the yield of extraction.
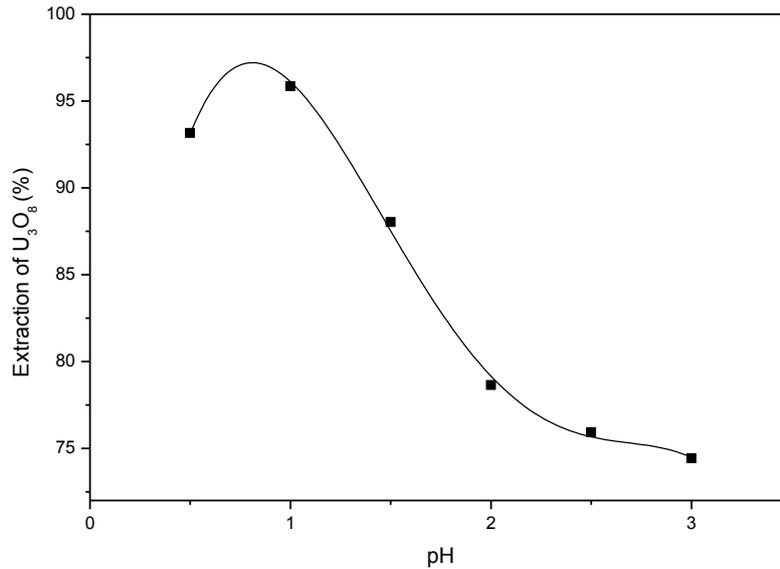
3.5. Effects of pH

In order to assess the influence of pH in different solid/liquid ratio, experiments were performed with 0.09 and 0.17 solid/liquid ratio respectively.

Figure 5. Effects of pH in the uranium extraction; 0.09 solid/liquid ratio and room temperature.

Figure 5 shows the results for 0.09 solid/liquid ratio, where there is a maximum extraction of uranium, after 4 hours of the procedure beginning, equal to 97.46% for pH 0.4 with a consumption of 767.1 kg of sulfuric acid per ton of residue. The curve has a downward trend in the percentage of extraction at pH higher than this.

Figure 6 shows that the maximum extraction occurs near pH 1.0 where 95.86% of the metal was extracted after 6 hours of leaching. For this experiment, the consumption of sulfuric acid was 576.2 kg per ton of residue. At pH above 1.0 there is an decreasing trend on the extraction of the metal, whose values remain around 90%.

**Figure 6. Effects of pH in the uranium extraction; 0.17
solid/liquid ratio and room temperature.**

Table 2 presents a summary of the uranium leaching experiments at 0.09 solid/liquid ratio and room temperature.

Table 2. Summary of results of tests with 0.09 solid/ liquid ratio

Acid leaching Testing	Feed calculated (gU/ton)	Residue (gU/ton)	Extraction U (%)	Consumption H_2SO_4 (kg/t)
pH= 0.4	2360.03	60	97.46	767.1
pH = 1.0	2644.84	130	95.08	662.5
pH = 2.0	2183.32	300	86.26	506.4
pH = 2.5	2030.48	430	78.82	503.8
pH =3.0	2119.60	740	65.09	389.5

The best result for the leaching of uranium at 0.09 solid/liquid ratio corresponds to the pH of 0.4 with 97.46% extraction. The consumption of sulfuric acid is equal to 767.1 kilograms per ton of residue. Another important result is related to the leaching at pH of 1.0 which presents 95.06% of uranium extraction and a consumption of 662.5 kilograms of sulfuric acid per ton of residue. The other leaching tests presented in Table 2 were not considered satisfactory as they indicate extraction lower than 90%.

Table 3 presents a summary of the uranium leaching experiments at 0.17 solid ratio and room temperature.

Table 3. Summary of results of tests with 0.17 solid/liquid ratio

Acid leaching Testing	Feed calculated (gU/ton)	Residue (gU/ton)	Extraction U (%)	Consumption H_2SO_4 (kg/t)
pH= 0.5	2808.58	192	93.16	643.9
pH = 1.0	2630.72	109	95.86	576.2
pH = 1.5	2473.84	296	88.03	586.2
pH = 2.0	2669.25	570	78.65	480.8
pH = 2.5	2574.90	620	75.92	539.3
pH = 3.0	2697.24	690	74.42	513.8

For the leaching tests at 0.17 solid/liquid ratio, the best result was attained at pH 1.0 where 95.86% of recovery of uranium was attained. The consumption of sulfuric acid was 576.2 kilograms per ton of residue. At pH 0.5 the percentage of extraction was lower, i.e., 93.16%, and the consumption of acid was 643.9 kg per ton of residue. Tests at pH values equal to or higher than 1.5 present less than 90% extraction. These values are much lower than that obtained at more acidic solutions.

4. CONCLUSION

It was noted that the pH value of the leaching experiments has a significant effect on the extraction of uranium as lower values of pH imply in more efficiency of the process. With regard to the solid/liquid ratio, its increase led to a slight decrease in the extraction of the metal desired. Regarding the time required for leaching, it was noted that around 2 hours is enough to attain maximum yield.

The study of the uranium recovery from the sludge generated in Caldas mine using the acid leaching technique indicated that it is possible to recover 96% of the uranium at pH 1.0 and 0.17 solid/liquid ratio with a consumption of sulfuric acid around 576.2 kg / ton of residue.

5. ACKNOWLEDGMENTS

6. REFERENCES

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