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Study in Laboratory of Aqueous Solutions Representing the Acidity of a Uranium Mine Under Decommissioning

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Abstract: The mine decommissioning process is associated to the mitigation of environmental impacts and recovery of degraded areas during the useful life of the unit. In the case of uranium mining, aspects concerning environmental radioprotection are necessary, thus avoiding increased human exposure to radiation and undesirable effects on the ecosystem. In order to adequately treat impacted areas, the possible form of management for environmental remediation will depend on the conditions of the particular mine. In the case of the Caldas Decommissioning Unit (UDC), mine acidity is a relevant issue, and the control of chemical elements in order to maintain the parameters defined by legislation must be continuously observed. Aiming to study strategic elements for the treatment of acid drainage water in the Caldas region, simulated solutions prepared in the laboratory, composed of Fe, Al and Mn, were proposed. It was possible to prepare a mixed solution with a concentration of these elements close to that found in the UDC, and representative of the acidity condition of the mine. The removal of elements by adsorption was also evaluated separately and together, verifying the influence of ions on the process. It was observed that the adsorbent material (RT) has a high adsorption power for iron, the ability to also adsorb manganese in concentrations close to those found in UDC, being influenced by the high aluminum content, which reduces its removal efficiency due to previous saturation. However, even in this case, the effectiveness of RT in treating acidic drainage waters is still evident, which can be enhanced by the combination of treatment methods. The study presented is especially relevant due to the conduct of activities that are representative of a real solution, but carried out in a controlled and simplified environment.

Keywords: uranium mine, acid mine drainage, environmental remediation, natural radionuclides.

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Estudo em Laboratório de Soluções Aquosas Representativas da Acidez de Mina de Urânio em Descomissionamento

Resumo: O processo de descomissionamento de mina está atrelado à mitigação de impactos ambientais e recuperação de áreas degradadas durante a vida útil da unidade. No caso de mineração de urânio, aspectos concernentes à radioproteção ambiental se fazem necessários, evitando assim o aumento da exposição humana à radiação e efeitos indesejáveis no ecossistema. De modo a tratar adequadamente as áreas impactadas, a forma de manejo possível para remediação de ambientes dependerá das condições da mina em particular. No caso da Unidade de Descomissionamento de Caldas (UDC), a acidez de mina é uma questão relevante, e o controle de elementos químicos de forma a manter os parâmetros definidos pela legislação deve ser continuamente observado. Com o objetivo de estudar elementos estratégicos ao tratamento de águas de drenagem ácida na região de Caldas, foram propostas soluções simuladas preparadas em laboratório, compostas por Fe, Al e Mn. Foi possível preparar uma solução mista com concentração destes elementos mencionados próxima àquela encontrada na UDC, e representativa da condição de acidez de mina. A retirada dos elementos por adsorção também foi avaliada separadamente e em conjunto, verificando a influência dos íons no processo. Observou-se que o material adsorvente (RT) apresenta elevado poder de adsorção para ferro, capacidade de também adsorver manganês em concentrações próximas às encontradas na UDC, sendo influenciado pelo elevado teor de alumínio, que reduz sua eficiência de remoção pela prévia saturação. No entanto, mesmo neste caso ainda se verifica a eficácia de RT no tratamento das águas de drenagem ácida, o que pode ser potencializado pela associação de métodos de tratamento. O estudo apresentado é especialmente relevante devido à condução de atividades que sejam representativas de uma solução real, mas realizadas em ambiente controlado e simplificado.

Palavras-chave: mina de urânio, drenagem ácida de mina, remediação de ambiente, radionuclídeos naturais.

1. INTRODUCTION

In 1982, the first ore extraction and processing unit for uranium production was inaugurated in Brazil [1], in a global context of growing demand for radioactive minerals for the production of nuclear energy. The Caldas Decommissioning Unit (UDC), which operated for 13 years, is located in the Poços de Caldas alkaline complex, in southeastern Brazil, where occurrences of uranium and thorium have been registered [1, 2].

Currently in the decommissioning process, the region is experiencing an environmental problem known as acid mine drainage (AMD), which affects several mining regions around the world. Due to deposits of radioactive minerals, the aggravating possibility of mobilization of metals such as uranium, through acid leaching, must be observed [2].

The AMD occurs due to the exposure of sulfide minerals to atmospheric air and rainwater, which leads to the release of large amounts of H^+ into the environment, lowering the pH of the water to levels even below 3 [3]. This acidity solubilizes metals in the water, increasing their availability in the environment, which can be worrying in terms of chemical toxicity and increased exposure to radiation, in the case of radionuclides involved [3, 4].

Conventional AMD neutralization systems use alkaline reagents such as lime, which increases the pH and remove metals in the form of hydroxides, forming a sludge as secondary residue. This process is currently used at UDC, requiring the addition of a large amount of lime for treatment [2, 4].

Among the elements that contribute to increasing the acidity of the drainage solution in mines are iron, aluminum and manganese. This occurs because, when soluble, Fe^{3+}, Al^{3+} and Mn^{2+} hydrolyze and release H^+, with the precipitation of these metals in the form of hydroxides and generation of additional H^+, as shown in Eq. 1 and Eq. 2, hindering the changes in pH that would occur in response to additions of OH^- [3].

$$Fe^{3+} + 2H_2O \rightarrow FeOOH\ (s) + 3H^+ \qquad \text{(Eq. 1)}$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3\ (s) + 3H^+ \qquad \text{(Eq. 2)}$$

In Brazil, CONAMA is the organization that limits the emission of effluents into water resources through its regulations, such as CONAMA Resolution Nº 430 of 05/13/2011 [5]. Knowing that according to regulations the effluent emission limit must be between pH 5-9, acidic effluents such as those from AMD face problems, in addition to the high concentration of dissolved metals, with emphasis on the established limits of manganese [4].

Plutonic and volcanic rocks have been tested to remove uranium from acid mine drainage and to increase the pH of these solutions. They constitute an effective alternative and may present a lower cost compared to conventional technologies for environmental remediation [6].

Therefore, it was proposed for this work to study simulated solutions, in the laboratory, based on concentration data obtained from the acid drainage waters of the UDC. The proposed solutions, containing the priority elements for studying the AMD problem, were also subjected to adsorption testing using a rock of volcanic origin as an adsorbent. The objective was to propose a solution that could represent the case of acid drainage, containing defined elements, to be used to predict the behavior of these elements without the need to use the AMD solution, relating the concentration of the adsorbent used to the metal content of interest to be removed that remains in the solution.

For this objective, different techniques were used to characterize the analytes. A preliminary analysis was performed by ICP-OES to evaluate the potential of the adsorbent material directly in the AMD waters. The prepared mixed solution was then characterized by ICP-MS/MS, mapping the concentration of other chemical elements present. Finally, atomic absorption, a simpler but more available technique, was used to study the relationship between the adsorbent added to the solution and the previously selected elements removed.

2. MATERIALS AND METHODS

Solutions were prepared in the laboratory with the aim of studying aspects of the particular case of the acid mine drainage process experienced at the Caldas Decommissioning Unit (UDC), Minas Gerais, Brazil (21°58S, 46°30W).

Initially, a preliminary study was carried out using two solutions – called BIA and BNF – collected at UDC, originating from acid drainage from a sterile pile. For this, 100 mL of each solution was placed in contact with 0.10 g of rocky adsorbent for cations, called RT. The adsorbent, which comes from a volcanic region in Japan and was provided by IQR Indústria Química, was used without additional preparation. It consists of a mixed material in the form of ash and rock fragments, with silicate as the main component [7], and a predominant granulometric fraction of fine sand based on ASTM D2487 – 11.

The subsequent analysis of the iron, aluminum and manganese content was carried out using the ICP-OES technique at the Poços de Caldas Laboratory - LAPOC/CNEN, in a Varian LIBERTY RL Sequential equipment, using three standards to compose the calibration curve for each element analyzed, and diluting the samples, when necessary, to perform the determination. The pH of the solutions was measured in a Digimed DM-22 equipment, with a resolution of 0.01, at room temperature.

For the purpose of this work, iron sulfate ($FeSO_4.7H_2O$), aluminum nitrate ($Al(NO_3)_3.9H_2O$) and manganese chloride ($MnCl_2.4H_2O$) were used as reagents. Then, 1 L of mixed solution (SOL MX) was prepared according to calculated to contain 2.14 $mg.L^{-1}$ of iron, 141.8 $mg.L^{-1}$ of aluminum and 83.0 $mg.L^{-1}$ of manganese, based on the concentrations found in the solutions from UDC. Then, 1 L was prepared for each solution containing only the precursors for iron and manganese, Fe and Mn, separately, with the same concentrations as SOL MX, totaling three simulated solutions. All used deionized water as diluent.

pH measurements of the solutions were determined using a Micronal B474 pH meter, with a resolution of 0.001, at room temperature.

The characterization of SOL MX regarding the concentration of the main elements present was carried out by ICP-MS/MS on Agilent 8800 equipment, with nitric acid being used to acidify the solutions and digest the samples. The solutions were calibrated using the 2A multi-element standard solution (SPEX, Horiba Jobin Yvon).

Next, adsorption tests were performed using the same rocky cation adsorbent, RT. Different concentrations of adsorbent (m1 = 0.05g; m2 = 0.10g; m3 = 0.20g; m4 = 0.50g; m5 = 1.0g; m6 = 2.0g all for 100 mL of solution) were tested, in order to verify the relationship between the concentration of the adsorbent used and the amount of iron and manganese that remained in the solution, when associated with aluminum. The material was placed in contact with the simulated solution for 24 hours, remaining on a bench shaker (Dubnoff bath, Nova Ética) during this time, at a temperature of 25 °C and with medium agitation at 150 rpm, and then the system was filtered.

The solution obtained after filtration was then analyzed by Atomic Absorption (AAS), using an XplorAA Dual equipment from GBC Scientific Equipment, with 7.00 mA lamp and length 248.30 nm for Fe, 5.00 mA lamp and length 279.50 nm for Mn, reading time 3.00s and 3 replicates, Linear Least Squares calibration parameter and air-acetylene flame.

3. RESULTS AND DISCUSSIONS

The determination of the pH of all solutions, including the UDC acid drainage solutions (BIA and BNF) was carried out at room temperature (25 °C) and the measured values are presented in Table 1.

Table 1 : pH of solutions prepared in the laboratory and collected in the mine.

SOLUTION	pH (± 0.005)
Fe	5.938
Mn	6.859
SOL MX	3.698
BIA	3.369
BNF	3.691

As can be seen, Fe and Mn solutions have a slightly acidic pH, and SOL MX has an acidic pH as observed for the drainage solutions in the mine, which was expected, since the solution was prepared from salts of the Al^{3+}, Fe^{2+} and Mn^{2+} cations, which hydrolyze in solution releasing H^+. The addition of the aluminum nitrate reagent is responsible for acidification in the case of the mixed solution. The pH of SOL MX, measured as 3.698, is close to that obtained by measuring the pH of BIA and BNF, respectively 3.369 and 3.691, as shown in Table 1.

Preliminary results obtained by ICP-OES showed that aluminum is adsorbed by RT in both BIA and BNF, and the pH of the solutions increased after the adsorption test, as shown in Table 2.

Table 2 : ICP-OES results for Al and pH of solutions after adsorption.

SOLUTION	Al CONCENTRATION [mg.L^{-1}]	% ADSORPTION	pH (± 0.05)
BIA	141.8	-	-
BIA + RT	116.3	18	4.37
BNF	123.4	-	-
BNF + RT	106.0	14	4.32

As can be seen in Table 2, just 1 $g.L^{-1}$ of RT is enough for aluminum adsorption above 10 % in both solutions. The pH of the solutions was also affected, going from around 3.37 (BIA) and 3.69 (BNF), as shown in Table 1, to 4.37 and 4.32, respectively (Table 2).

Under the conditions initially studied, there was no evidence of manganese adsorption, and iron presented a concentration below the detection limits after the test, indicating that it may have been completely adsorbed. Knowing that both the charge and the ionic radius of the cations are different, these factors may have influenced the selectivity of the ions, with Mn^{2+} being the metallic cation that has the largest size and least interaction in solution in relation to the others studied. Iron, because it is in a lower concentration than the others, can have its adsorption proportionally favored, allowing a small adsorbed fraction to represent almost the entire component present in solution.

Thus, the proposed work sought to separately investigate the adsorption potential of iron and manganese, and associated with aluminum, through simulated solutions. In order to evaluate a condition close to the reality of acid drainage samples, the highest concentrations identified of these elements among the samples were used as a parameter to calculate the mass of reagent required to prepare the solutions.

The prepared SOL MX solution was calculated taking into account only the amount of ions obtained from the elements Fe, Al and Mn from their corresponding salts (as described in the Materials and Methods section), when dissolved in deionized water. Therefore, the same reagent mass used to prepare the isolated Fe and Mn solutions was used to prepare the mixed solution. Thus, the characterization of SOL MX in order to specify its composition and measured concentration of the main elements was carried out via ICP-MS/MS. These results can be seen in Table 3.

According to what can be observed in Table 3, the focus elements of this study present a concentration determined by ICP-MS/MS lower than that calculated for their preparation:

0, 130 mg.L^{-1} for Fe, 116.0 mg.L^{-1} for Al and 72.0 mg.L^{-1} for Mn, and the presence of other elements can also be observed.

Table 3 : Concentration of elements identified in SOL MX by analysis via ICP-MS/MS.

ELEMENT	CONCENTRATION [µg.L^{-1}]	RSD [%]
Na	1120.2	3.0
Mg	270.2	7.6
Al	116047.7	2.1
Ca	537.0	3.6
Mn	72012.1	0.5
Fe	129.7	1.4
Cu	6.8	1.8
Zn	493.9	3.7
Ba	13.4	3.5
Pb	6.0	0.7

% RSD or relative standard deviation is a value obtained directly from the analysis.
Standard deviation (SD) can be calculated by multiplying the measured value (mean) and RSD.

This characterization is particularly important to have a description of possible interferences present in the simulated solution that would affect the final response of removing the focus elements. As the concentration of iron is much lower in relation to that of aluminum and manganese, there is a greater change in the value obtained for it, highlighting that for manganese and aluminum the concentrations defined by ICP-MS/MS are as high as those intended. The difference obtained for the concentration mainly of iron may be related to its precipitation, as it was already in a reduced concentration in relation to the other elements studied, or it may even be the result of ionization interference in the ICP analysis.

The simulated solutions were placed in contact with the selected adsorbent, in order to determine the relationship between the concentration of the added adsorbent and the amount of iron and manganese that remained in the solution after the test, when in the presence of a large amount of aluminum (> 100 mg.L^{-1}). The adsorbent, RT, is a rocky material with high cation adsorption capacity, coming from a volcanic region in Japan and composed mainly of silicates, with a predominant granulometry of fine sand, as described in the methodology. The results obtained by AAS are shown in Table 4.

Table 4 : Results obtained by AAS for the adsorption test.

RT ADDED	Fe ISOLATED SOLUTION [mg.L-1]	% RSD	Mn ISOLATED SOLUTION [mg.L-1]	% RSD	Fe SOL MX [mg.L-1]	% RSD	Mn SOL MX [mg.L-1]	% RSD
0	1.63	2.20	80.00	1.80	2.03	2.50	83.88	0.14
m1	0.00	-	77.50	1.71	1.90	0.82	83.63	1.56
m2	0.00	-	76.00	1.64	1.84	1.02	84.25	0.86
m3	0.00	-	74.25	0.23	1.84	6.67	85.13	0.40
m4	0.00	-	59.63	0.32	1.62	3.87	85.25	0.92
m5	0.00	-	39.88	2.06	1.15	7.16	83.88	0.88
m6	0.00	-	41.63	0.42	0.00	-	60.13	1.17

The results showed that while the concentration of RT for m1 (0.5 g.L^{-1}) is already enough to adsorb all the iron present in the isolated solution, only after adding m4 (5 g.L^{-1}) of RT to the isolated manganese solution is it significantly removed, reaching approximately 50% removal for m5 (10 g.L^{-1}). For the mixed solution, adsorption is affected by the presence of aluminum, and iron becomes completely adsorbed only at m6 (20 g.L^{-1}). In this case, the iron concentration gradually decreases as the mass of added adsorbent increases, with approximately half of its initial concentration being reached in condition m5. According to the analysis of manganese in SOL MX, only after m6 can adsorption be evident, at around 30%. Thus, it is observed that the exchange capacity of the adsorbent material is probably affected by the higher ionic strength of the medium in SOL MX, or even by interaction properties between the Al, Fe and Mn ions. Thus, the adsorption yield is lower for the mixed solution.

Based on the results obtained, a polynomial regression was performed, both for Fe and Mn, with the objective of estimating the remaining concentration of the element y in the mixed solution (in mg.L^{-1}), according to the concentration of adsorbent added x in g.L^{-1}. The results of the determined equations, as well as their respective coefficients of determination, are shown below:

Fe:

$$y = -0.0017x^2 - 0.064x + 1.9645$$

$$R^2 = 0.997$$

Mn:

$$y = -0.1143x^2 + 1.1328x + 83.303$$

$$R^2 = 0.997$$

The equations model the behavior obtained for the system in the adsorbent addition range between 0 and 20 g.L^{-1}. From the values of R^2 obtained, it can be seen that the model fits well with the observed values. The results indicate that the rate of variation of the phenomenon is not constant; that is, the remaining concentration of solute in the solution does not vary linearly as the concentration of adsorbent that was initially added increases. For the systems studied, as the mass of RT added increases, the impact on the adsorption of the solute intensifies. This behavior may be the result of the more intense interaction of the adsorption sites with the solute, due to the additional sites resulting from more mass of the adsorbent in the medium, leading to a proportionally greater removal of solute; in addition to more available areas, there is greater proximity between the solute molecules and the areas, which may facilitate the interaction.

This study allows a more assertive choice of the RT mass required for the selective adsorption of the ions of interest, at acidic pH such as that found in acid mine drainage conditions.

4. CONCLUSIONS

According to the analysis of real acid mine drainage solution at UDC and bibliographic research, it was possible to determine the priority chemical elements for studying the problem situation. Thus, although other elements are present, aluminum, iron and manganese were selected to compose the simulated solution, in concentrations established based on the real solution. In this way, solutions were reproduced in the laboratory, with the elements isolated and together, which proved to be appropriate for investigating the adsorption of strategic components. The solution of the elements together presented an acidity condition close to that found in the UDC decantation basins ($3 < pH < 4$). Analysis of the pH in the UDC acid drainage solutions after the adsorption process showed a decrease in acidity, which was a desirable condition. In the isolated solutions, iron was completely removed for $m1 = 0.05$ g. 100 mL^{-1} of adsorbent, and manganese for a maximum of $m5 = 1.00$ g. 100 mL^{-1}, with approximately 50% withdrawal. Polynomial regression equations were proposed to relate the mass of adsorbent added and the remaining concentration of Fe and Mn in the proposed mixed solution. The relevance of this work lies in the safe conduct of auxiliary studies that aim to contribute to the decommissioning process, which began in the region after the stoppage of uranium exploration and production activities in 1995.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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