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FLUORIDES EVALUATION IN SPENT POT LINER: TOXICITY CHARACTERISTIC LEACHING PROCEDURE LIMITATIONS

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ABSTRACT

The spent potliner (SPL) is a solid waste generated in the process of aluminum production and is considered hazardous because of its fluoride and cyanide content. The purpose of this study was to analyze the SPL fraction with low cyanide coming from Aluminio Brasileiro S.A. (ALBRAS). For all the pots studied the pH of the spent potliner (SPL) was very high and ranged from 10 to 11.80. The total fluoride content determined at high pH varied from 5.13 to 11.41 %, while the total fluoride determined in leached fluid at pH 5.0 had low values that ranged from 0.26 to 3.46 %, indicating the low solubility of waste fluorides at low pH values. With leaching fluid above pH 12, the total fluoride content varied from 6.45 to 9.39 %. The experimental results indicate that the Brazilian Standard NBR 10.004, based on leaching at pH 5.0 is not adequate for classification of hazardous waste, since it underestimates fluoride content.

Keywords: Fluoride, Spent potliner, Solid Waste, Ion Selective Electrode, Leaching Test.

RESUMO:

O resíduo gasto de cuba (RGC) é um resíduo sólido gerado no processo de produção de alumínio e é considerado perigoso devido ao seu teor de fluoreto e cianeto. O objetivo deste estudo foi analisar a fração do RGC com baixo teor de cianeto proveniente da empresa Alumínio Brasileiro S. A. (ALBRAS). Para todas as cubas estudadas o pH do RGC foi muito elevado e variou entre 10 e 11,80. O teor de fluoretos totais determinado em pH alto variou de 5,13 a 11,41 %, enquanto que o teor de fluoretos totais determinado em fluido de lixiviação com pH 5,0 teve valores baixos que variaram de 0,26 a 3,46 %, indicando a baixa solubilidade dos fluoretos do resíduo em baixos valores de pH. Com fluido de lixiviação em pH acima de 12, o teor de fluoretos totais variou de 6,45 a 9,39 %. Os resultados experimentais indicam que a Norma Brasileira NBR 10.004, com base na lixiviação em pH 5,0, não é adequada para a classificação de resíduos perigosos, pois subestima o teor de fluoretos.

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INTRODUCTION

In the process of aluminum production, alumina is dissolved in cryolite in electrolytic cells, called pots, which consist of a steel shells lined with carbon. A number of pots, more than 100, are arranged in series to form a potline. In a typical aluminum production plant there are several potlines. The pots contain a molten electrolyte consisting primarily of cryolite (Na_3AlF_6) and operate at approximately 930 to 1000 °C. Other materials are added to the electrolyte to improve the efficiency of the operation or to reduce power consumption, such as alumina, aluminum fluoride, sodium fluoride, soda ash, calcium fluoride, lithium carbonate and magnesium oxide.

The hearth or lining of the cell is composed of carbon, which is backed by insulation and contained within a steel container called a potshell. The carbon portion of the lining serves as the cathode and contains the molten electrolyte. The carbon lining is composed of prefabricated carbon blocks joined together by a carbon paste, which is hydraulically rammed in the seams between the carbon blocks. The sidewalls of the lining are typically formed with carbon paste, but may contain prefabricated carbon blocks. The carbon material within the lining, both blocks and paste, is predominantly anthracite-based material. It may contain some graphite to improve its electrical and thermal properties. Insulation packages for a cell are mostly of insulating and refractory bricks.

During the life of the cathode and its cell lining, the carbon and insulating materials become impregnated with fluoride-containing salts. As the addition of salts continues, the integrity of the lining is adversely affected. Sodium, in particular, can actually intercalate within the crystalline lattice of the carbon materials, causing distortion and stresses within the lining. The insulating materials become more thermally conductive as they are impregnated by these fluoride salts. Failure can occur by cracking or excessive heaving of the lining. When these failures occur, the cell is taken off the line and the cathode lining material is removed from the potshell by mechanized digging equipment. This spent cathodic material is referred to as spent potliner (SPL). The life cycle of a cathode varies about three to about ten years. Since there are numerous pots located at a single aluminum reduction plant, the decommissioning and relining of cathodes is a continuous process. In addition to containing fluoride salts, SPL contains cyanides that are formed by the entrance of air through openings in the potshell and subsequent reaction of nitrogen with the carbon lining. Due to the fluorides and cyanides content, spent potliner was listed by the Environmental Protection Agency (EPA) on Sep. 13, 1988 (53 Fed. Reg. 35412) as a hazardous waste (K088) and it is not allowed to be deposited on normal deposits. There has been proposed a number of methods for treatment this waste of such way it can be safely deposited [1,2] . Alumínio Brasileiro S. A. (ALBRAS) industry, located at Barcarena, Pará state, produces about 350.000 tons per year of aluminum and generates several tons of spent potliner which has been maintained in controlled deposits. Seeking for a more viable destination for this waste, the SPL was separated in two fractions, one of which composed of material without the cathode, with low cyanide content. The purpose of this work was to determine the fluoride content of this SPL fraction following the Brazilian Standards and discuss critically the results considering the limitations of the toxicity characteristic leaching procedure.

MATERIALS AND METHODS

a) Sampling and Sample Preparation

The waste to be studied was arranged in piles and the material was collected by simple random sampling [3-5]. The waste mass collected was fragmented and homogenized, random sampling again was used. This material was taken to laboratory and was prepared for analysis according to extraction procedure requirements.

b) pH Measurement

Waste sample pH was measured by electrometric procedure according to the EPA Method 9.045C [6], where 20 g of solid sample was placed in a 50 ml beaker, added 20 ml of reagent water, and at 25 ± 1 °C stirred the suspension for 5 minutes. The waste suspension was let stand for about 15 minutes, filtered off aqueous phase, and measured the pH.

c) Leaching and Solubilization Tests

The leaching and solubilization tests were carried out according to the procedures established by Brazilian Standards NBR 10.005 [7] and NBR 10.006 [8], respectively. In the leaching test procedure 100 g of the waste were mixed with a leaching fluid at pH = 5,0 ±0,2. The solubilization test was done by mixing 250 g of the solid waste with 1.000 ml of distilled water and leaving it rest for 7 days. Considering the waste pH and the low solubility of the waste fluorides in acidic solutions, the leaching tests were also carried out under a more aggressive conditions, where the pH of the leaching fluid was maintained above 12 during the experiments.

d) Total Fluoride Extraction

Total fluoride extraction was done by alkaline fusion, where a sample of 0.5 g of the solid waste was mixed with 15 ml of 10 % (w/w) $Ca(OH)_2$ solution and heated until completely dry. To this mixture was added 3 g of solid NaOH and heated to 800 °C for 30 minutes. After cooling, 40 ml of distilled water were added, heated gently until complete dissolution. Then 40 ml more of distilled water were added and distilled [9, 10].

e) Fluoride Determination

The extracts obtained from the steps c) and d) were distilled following the procedure as established by the Standard Methods [11] and the distilled fluorides evaluation carried using the ion selective electrode method, instrument Orion Model 96-09 [12].

RESULTS AND DISCUSSION

The pH of the solid wastes generated by pots with different operation times is presented in the Figure 1.

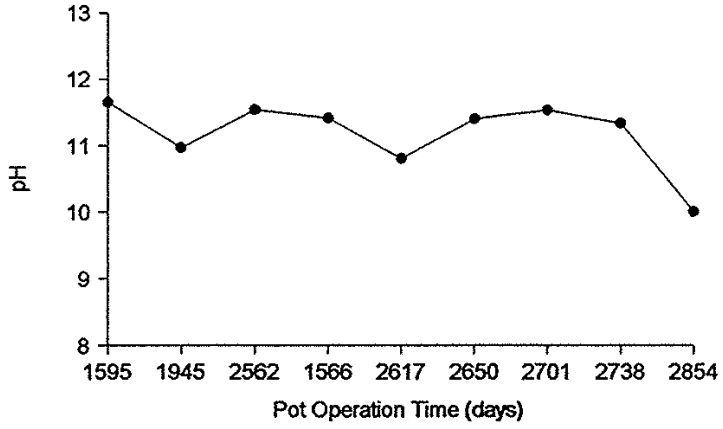

Fig. 1 - Behavior of the inorganic fraction of SPL pH as a function of the pot operation time (days)

The SPL total fluorides, fluoride concentrations of the extracts obtained by using a leaching fluid with pH = 5,0 and pH > 12 and fluoride concentrations of the extract obtained from the waste solubilization as a function of the pot operation time are presented in the Figure 2.

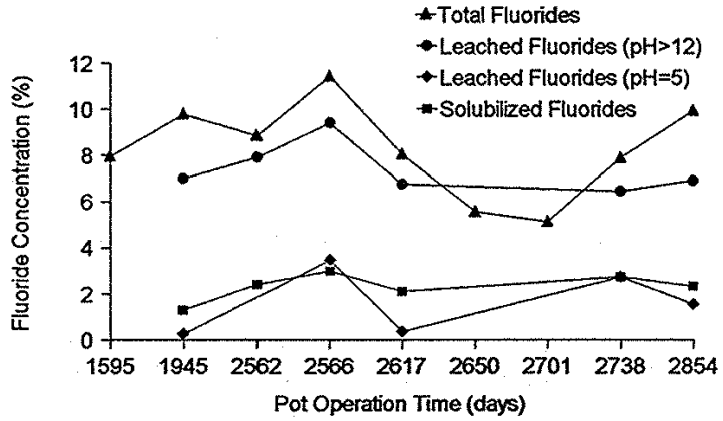

Fig. 2 – Changes of total fluoride, leached fluorides (pH > 12), leached fluorides (pH = 5) and solubilized fluorides concentrations (% w/w) as a function of the pot operation time (days).

From the results shown in the Figure 1 it can be observed that the SPL pH is very high, changing from 10 to 11.80, with an average value of 11.18 and very little oscillation with operation time of the pots. These very high pH values influenced the results of the leaching and solubilization tests.

In Figure 2 it is observed that the total fluoride concentration of the waste changed from 5.13 to 11.41 %, with an average value equal to 8.29%, but from the results obtained for the leaching test carried out according to Brazilian Standard NBR 10.005, where the extraction fluid was maintained at pH = 5.0, the leached fluoride concentration changed from 0.26 to 3.46 %, with an average value equal to 1.67 %, much lower than the actual fluoride content of the waste. These values are very close to those ones obtained from the solubilization tests, where the average value was 2.33%. This indicates that at low pH values the fluorides of this waste have low solubility.

Under a more aggressive conditions, where the leaching fluid pH was maintained above 12, it can be observed the leached fluoride concentration varying from 6.45 to 9.39 %, with an average value of 7.41 %. These values are close to those obtained for total fluoride, indicating the high solubility of the waste fluorides under alkaline conditions.

According to the Brazilian Standard "Solid Waste Classification - NBR 10.004" a fluoride content above 150 ppm or 0.015 % (w/w) of an extract obtained following the procedure established by NBR 10.005 would classify the waste as hazardous. From the results presented in the Figure 2 it can be seen that some pots could have their waste classified as non hazardous, but based on the average value, all of them would be hazardous. If the waste is non- hazardous, it is necessary to check if it is inert or not. The extract obtained from the solubilization tests (NBR 1.006) must have a fluoride concentration below 1.5 ppm. From the results it can be seen that none of the pots studied generated an inert waste.

From the leaching test results it can be concluded that the spent potliner studied as a whole is a hazardous waste, but this is not a safe classification for some pots due to the proximity between the concentration values obtained for the waste and the limit established by Brazilian Standards. These doubts only appeared because the leaching test underestimated the waste fluoride content, as it was shown by comparing the total and leached fluorides. Moreover, considering the pH of the waste, the leaching under natural environment conditions would be different from that done with a leaching fluid at pH equal to 5. The leaching procedure as established by Brazilian Standard (NBR 10.005) is not an adequate test for the evaluation of spent potliner fluoride contents.

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