

## Characterization of inorganic fraction of spent potliners: evaluation of the cyanides and fluorides content

B.I. Silveira\*, A.E. Dantas, J.E. Blasquez, R.K.P. Santos

*Chemical Engineering Department, Federal University of Pará, Pará, Brazil*

Received 9 February 2001; received in revised form 5 July 2001; accepted 9 July 2001

---

### Abstract

Spent potliner (SPL) is a solid waste generated by the aluminum industry during the manufacture of aluminum metal in electrolytic cells. Initially the electrolytic cell liners comprise of graphite and carbonaceous materials, but after several years of operation, the liner materials deteriorate and must be removed from the cells. Because of the presence of fluoride and cyanide in the SPL, the US Environmental Protection Agency (USEPA) has listed the materials as a hazardous waste. The purpose of this work was to characterize the extent of leaching of cyanides and fluorides from SPL, as a function of the number of years the material was present in an operating electrolytic cell. At Alumínio Brasileiro S.A. (ALBRAS) plant, SPL was separated into two fractions: a carbon component and an inorganic part. Inorganic materials from nine pots, about 28 tonnes per pot, were examined in this study. When placed in water at a ratio of 20 g solid to 20 ml of water, the pH for all samples varied from 10 to 11.8. The total measured fluoride content of the solid samples varied from 5.13 to 11.41%. However, when leached at a pH of 5, the dissolved fluoride was equivalent to only 0.26–3.46%. With a pH of 12 in the leachate solution, the dissolved fluoride was equivalent to 6.45–9.39%. The data show that the fluorides of the waste are more soluble in basic solutions, and when leached at a pH of 12 are much closer to the actual fluorides content. For the same samples, the dissolved quantity of cyanide was equivalent to 4.34–27.33 ppm, with an average of 13.26 ppm. For all the samples studied, there did not appear to be a correlation between the fractions of fluoride and cyanide leached from the samples and the operating life of the potliner materials. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Fluoride; Cyanide; Spent potliner; Solid waste; Ion selective electrode; Leaching test

---

\* Corresponding author. Fax: +55-91-211-1291.

*E-mail address:* inacio@ufpa.br (B.I. Silveira).

## 1. Introduction

In the process of aluminum production, alumina is dissolved in cryolite in electrolytic cells, called pots that consist of steel shells lined with carbon. A number of pots, usually more than 100, are arranged in series to form a potline. At a typical aluminum production plant there are several potlines. The pots contain a molten electrolyte consisting primarily of cryolite ( $\text{Na}_3\text{AlF}_6$ ) and operate at approximately 930–1000°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 a 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 pre-fabricated carbon blocks joined together by a carbon paste, which is rammed hydraulically into the seams between the carbon blocks. The sidewalls of the lining typically are formed with carbon paste, but may contain prefabricated carbon blocks. The carbon material within the lining, both blocks and paste, predominantly is 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.

Over the life of the cathode and its cell lining, the carbon and insulating materials become impregnated with fluoride-containing salts. As the infiltration of salts proceeds, the integrity of the lining is affected adversely. Sodium, in particular, actually can intercalate within the crystalline lattice of the carbon materials, causing distortion and stresses within the lining. The insulating materials become more thermally conductive as these fluoride salts impregnate them. Failure can occur by cracking or excessive heating of the lining. When these failures occur, the cell is taken off-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 typically varies from about 3 to 10 years. Because there are numerous pots located at a single aluminum reduction plant, decommissioning and relining of cathodes is a continual process. In addition to containing fluoride salts, SPL contains cyanides that are formed by the infiltration of air through openings in the potshell and subsequent reaction of nitrogen with the carbon lining. A review of the literature shows the composition of SPL to be highly variable (e.g. cyanide, fluoride, organics and metals), but the components of greatest concern environmentally are cyanide and soluble fluoride salts. Due to the concentrations of fluorides and cyanides in spent potliner, and the tendency to leach in contact with water, the US Environmental Protection Agency (USEPA) listed the materials on 13 September 1988 (53 Fed. Reg. 35412) as a hazardous waste (K088) under 40 C.F.R., Part 261, Subpart D.

The aluminum industry has long recognized the environmental liability of SPL and is pursuing many options for treatment and/or disposal. These options include landfilling, recycling as a feedstock in other industries, such as the steel, cement, aluminum, or mineral wool industries, fluidized bed combustion, cryolite recovery, pyrohydrolysis, pyrosulfolysis and others. Recycling through other industries is an attractive and proven option; however, classification of SPL as a hazardous waste has greatly discouraged other industries from utilizing SPL, due to the burdensome and expensive environmental regulations [1,2].

Alumínio Brasileiro S.A. (ALBRAS), located at Barcarena, Pará state, Brazil, has stored spent potliner waste in controlled deposits. Seeking a reduction in the quantity of this waste, SPL of each pot was separated into two fractions: one fraction, about 25 tonnes, contained the majority of the carbonaceous material, while the other, about 28 tonnes, consisted primarily of inorganic components. The purpose of this work was to characterize the inorganic fraction, including the leachability of cyanides and fluorides, and some metals as a function of the pot operation time.

## 2. Materials and methods

### 2.1. 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 was again used. This material was taken to laboratory and was prepared for analysis according to extraction procedure requirements.

### 2.2. 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 stirred the suspension for 5 min at  $25 \pm 1^\circ\text{C}$ . The waste suspension was let to stand for about 15 min, filtered off aqueous phase and measured the pH.

### 2.3. Total cyanide

Total cyanide analysis was performed according to the procedure established by EPA SW-846 Method 9.010B [7] followed by an evaluation using a selective ion electrode method, instrument Orion Model 94-06 [8].

### 2.4. Total and leachable fluorides

Total fluoride extraction was done by alkaline fusion, where 0.5 g of the solid waste was mixed with 15 ml of 10% (w/w)  $\text{Ca}(\text{OH})_2$  solution and heated until completely dry. To this mixture was added 3 g of solid NaOH and heated to  $800^\circ\text{C}$  for 30 min. After cooling, 40 ml of distilled water were added and heated gently until complete dissolution. Then 40 ml more of distilled water were added and distilled [9,10]. Leachable fluorides were determined using two methods. In the first one, EPA SW-846 Method 1.311 [11] was used and in the second, which considered the waste pH and low solubility of the fluorides in acidic solutions, leaching tests were carried out in a more aggressive conditions, where the extraction liquid pH was maintained above 12 during the experiments. Extracts obtained from the above steps were submitted to a distillation procedure as established by standard methods [12] and the distilled fluorides evaluation carried out through the ion selective electrode method, instrument Orion Model 96-09 [13].

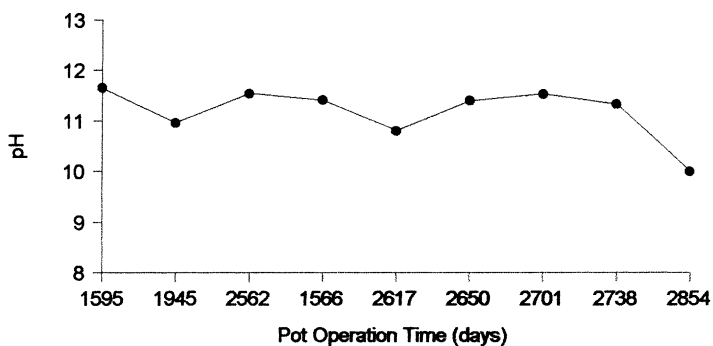


Fig. 1. Behavior of the inorganic fraction of SPL pH as a function of the pot operation time (days).

### 2.5. Metal analysis

The analysis of Na, Fe, Al and Ca was performed according to the procedure established by EPA SW-846 Method 7000<sup>A</sup> — “Atomic Absorption Methods” [14] using the instrument VARIAN 2000.

## 3. Results

The pH of the solid wastes generated by pots with different operation times is presented in Fig. 1. In Fig. 2 the behavior of the leachable cyanide concentrations (ppm) is presented as a function of pot operation time.

The SPL changes of total and leached fluoride concentrations (g of fluoride/100 g of SPL inorganic fraction) of the extracts obtained by using a leachate fluids with pH > 12 and 5.0, respectively as a function of pots operation time are presented in Fig. 3.

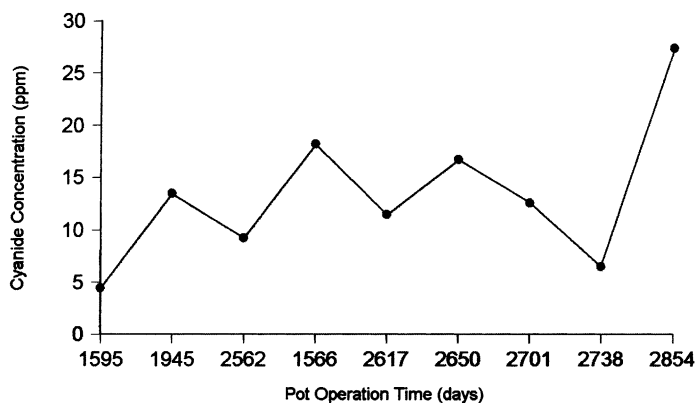


Fig. 2. Change of the leachable cyanide concentration (ppm) as a function of pot operation time (days).

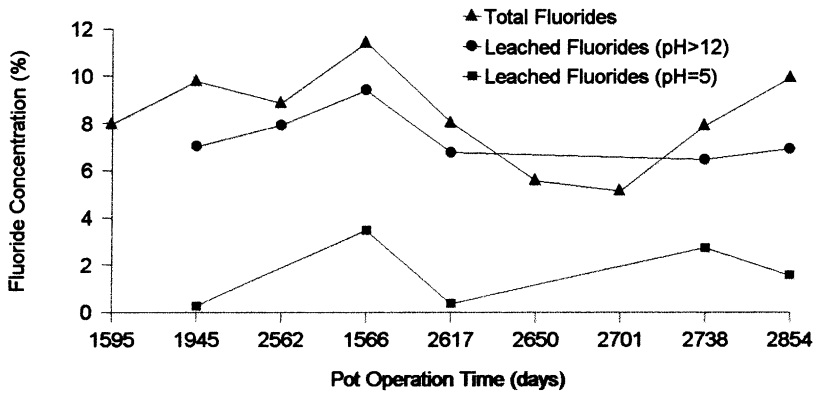


Fig. 3. Changes of total fluorides, leached fluoride obtained by using a leachate fluid with pH > 12 and leached fluoride obtained by using a leachate fluid with pH = 5.0 concentrations (% w/w) as a function of the pot operation time (days).

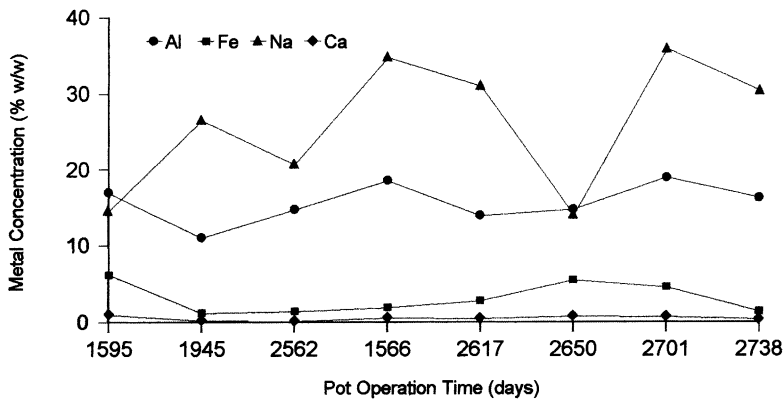


Fig. 4. Change of the concentrations (% w/w) of the metals Al, Fe, Na and Ca as a function of the pot operation time (days).

In Fig. 4 the behavior of the metals Fe, Al, Na and Ca concentrations (% w/w) is presented as a function of pot operation time, where the total concentration average values are: Al, 15.57%; Fe, 3.05%; Na, 25.89%; Ca, 0.48%.

#### 4. Discussion

From the results shown in Fig. 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 along the pot operation time. These very high pH values influenced the fluoride salts behavior during the leaching tests as it will be shown later.

In Fig. 2, it is observed that the cyanide extract concentrations changed from 4.34 to 27.33 ppm, with an average of 13.26 ppm.

The results presented in Fig. 3 show that the total fluoride concentrations of the waste changed from 5.13 to 11.41%, with an average value equal to 8.29%, and the leached fluoride from a leachate fluid with pH at 5.0 changed from 0.26 to 3.46%, with an average value equal to 1.67%. The leached fluoride concentrations in acidic solutions are much lower than the total fluoride content of the waste. In the same figure, the results show that in a more aggressive condition, where the leachate fluid pH was maintained above 12, the leached fluoride concentrations varied from 6.45 to 9.39%, with an average value of 7.41%. These values are close to those obtained for total fluorides, indicating the high solubility of the waste fluorides in alkaline conditions.

These results also show that the solubility of fluoride ions is largely governed by the leachate fluid pH and metal ions present in the SPL samples.

In Fig. 4, the change of the metals Al, Fe, Na and Ca concentrations as a function of the pot operation time is shown.

From all of the results presented, we concluded that there is no proportionality between the concentration of the components studied and the pots operation time.

It also can be concluded that the leaching procedure as established by EPA SW-846 Method 1.311, with leachate fluid pH at 5.0, underestimates the fluoride mobility from spent potliner inorganic fraction, since fluoride is more soluble under highly alkaline conditions. This problem has already been raised by USEPA and by 12 July 2000, when this research was under way, it published new recommendations for fluoride analysis, from when it started using deionized water as leaching fluid in the toxicity characteristic leaching procedure [15].

## Acknowledgements

This paper represents part of the work developed by the project “Characterization of ALBRAS Spent Potliner” financially supported by Alumínio Brasileiro S.A. (ALBRÁS) Industry through an agreement with the Federal University of Pará, Brazil.

## References

- [1] F. Chania, E. Eby, Best Demonstrated Available Technology (BDAT) Background Document For Spent Aluminum Potliners-K088, US Environmental Protection Agency Office of Solid Waste, Washington, DC, 31 May 2000.
- [2] US Environmental Protection Agency, Office of Research and Development, Characterization for Spent Potliners from the Primary Reduction of Aluminum, US Environmental Protection Agency, Cincinnati, OH, 16 April 1991.
- [3] Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (SW-846), 3rd edition, US Environmental Protection Agency, Washington DC, 1995 (Chapter 9).
- [4] L.H. Keith, Principles of Environmental Sampling, 2nd edition ACS, Washington DC, 1996.
- [5] Associação Brasileira de Normas Técnicas (ABNT), NBR 10.007-Amostragem de Resíduos, 1987.
- [6] Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (SW-846), Method 9.045C — Soil and Waste pH, US Environmental Protection Agency, 3rd edition, Washington DC, 1995.

- [7] Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (SW-846), Method 9.010B — Total and Amenable Cyanide: Distillation, US Environmental Protection Agency, 3rd edition, Washington DC, 1992.
- [8] Orion Model 94-06 and Model EA-920 Expandable ion analyzer, Cyanide Electrode Instruction Manual, Orion Research, Boston, MA, 1986.
- [9] N.R. Mcquarker, M. Gurney, *Anal. Chem.* 49 (1) (1977) 53–56.
- [10] Fluxo de Análise no 365/ ALBRÁS, Determinação de Flúor Total em Criolita.
- [11] Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (SW-846), Method 1.311 — Toxicity Characteristic Leaching Procedure, US Environmental Protection Agency, 3rd edition, Washington DC, 1992.
- [12] A.E. Greenberg, L.S. Clesceri, R.R. Trussell, *Standard Methods for the Examination of Water and Wastewater*, 18th edition, American Public Health Association, Washington DC, 1992.
- [13] Orion Model 94-09 Fluoride Electrodes and Orion Model 96-09 Combination Fluoride Electrodes, Instruction Manual, Orion Research, Boston, MA, 1992.
- [14] Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (SW-846), Method 7000<sup>A</sup> — Atomic Absorption Methods, Method 770 Sodium, Method 7380 Iron, Method 7140 Calcium and Method 7020 Aluminum, US Environmental Protection Agency, 3rd edition, Washington DC, 1995.
- [15] *Federal Register*, Vol. 65, No. 134, Wednesday, 12 July 2000, Proposed Rules US Environmental Protection Agency.