

Chemical treatment of spent carbon liners used in the electrolytic production of aluminum

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Abstract

Chemical cleaning methods were developed for the removal of leachable hazardous cyanide and fluoride impurities from spent carbon liners used in aluminum metal production. Cyanide can be destroyed by treatment with NaOCl solutions at near-neutral pH. Fluoride can be removed by treatment with solutions of strong acids, e.g., 0.5 M H₂SO₄. This treatment is more effective at elevated temperatures (e.g., 80 °C). The acid used in chemical cleaning can be treated in order to remove extracted fluoride by passing it through an alumina bed.

Keywords: Aluminum production; Cyanide; Fluoride; Carbon liners; TCLP; Leaching

1. Introduction

Aluminum metal is most commonly produced using the Hall–Heroult process [1]. This process involves the electrolysis of alumina, dissolved in a sodium aluminum fluoride electrolyte, in a cell having carbon electrodes and carbon lining used to transmit current from the cathodic collector bar and to contain the molten aluminum product and alumina-containing electrolyte. This lining usually consists of baked carbon blocks containing anthracite and coal tar pitch. Over several years of use, the carbon liners develop stress as a result of a combination of mechanical stresses and penetration of electrolyte. At this stage, it is necessary to remove the spent liner and replace it by new carbon material. Various strategies have been used in the disposal of the spent liners. Instead of landfilling, which was recognized as wasteful, many companies crushed the spent liners and recovered the fluoride and carbon material. Over the past 15 years, considerable portions of the spent liner material

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have been used in cement plants as a coal substitute, and in steel mills and cupolas as a source of energy and chemical value. However, the spent material often contains excessively high concentrations of contaminants. One contaminant of particular concern is fluoride, originating from the penetration of the molten electrolyte into the carbon [2, 3]. Another important contaminant is cyanide, formed as a result of a reaction involving metallic sodium diffusing into the carbon material, the carbon itself, and atmospheric nitrogen penetrating into the material [2, 3]. In typical situations, the spent carbon liners may contain as much as 8–10% fluoride and up to 0.2% cyanide. The corresponding concentrations of fluoride and cyanide in leachates obtained upon determination of the extent of leaching of these species from spent liners using the Toxic Characteristic Leaching Procedure (TCLP) [4, 5] may reach up to 1000–2000 mg/l and 10–50 mg/l, respectively, depending on the technology of the electrolytic cells. Based on the fact that significantly high concentrations of these contaminants are present in the spent liners, these liners qualify as hazardous wastes according to EPA standards and may require the use of alternative methods of liner disposal [6] or control and treatment of the leachates formed as a result of contact between the liners and water [7]. Indeed, techniques involving incineration and immobilization in oxide byproducts of alumina purification have been proposed.

The approach attempted in the present study, involving chemical cleaning of the spent carbon, is intended to permit reduction of leachable contaminant concentrations to non-hazardous levels which would permit direct disposal of the liners or reprocessing of the cleaned material.

2. Experimental

The present studies were conducted on spent carbon liner material obtained from two industrial manufacturers of aluminum metal. The samples were in the form of irregular lumps weighing several grams each (typical dimension ranging up to 9.5 mm), and they were used without pulverization or cleaning. The anthracite used to make the liner material used in the present work originated in Pennsylvania or the Soviet Union. Modified TCLP tests were carried out according to a version of the EPA protocol described in Ref. [4] using scaled-down sample weight and leachant volume, original pieces of the sample, and a slightly shorter duration than the TCLP procedure. In each of the present tests, a quantity of 20 g of sample was leached in 800 ml of extraction fluid contained in a plastic bottle and rotated end-over-end at 30 rpm over a period of 18 h. The solid sample was then separated from the leachate by means of a glass fiber filter under mild vacuum and analyzed to determine the cyanide and fluoride concentrations. In the fluoride studies, the slightly acidic extraction fluid of Ref. [4] (0.1 M acetic acid/sodium acetate buffer at pH 4.93) was used as it is more effective in leaching fluoride than deionized water and as pH values lower than 4.93 are unlikely to be encountered in the disposal of the spent liner material. In the cyanide studies, deionized water was used, because the use of acidic leachants causes loss of cyanide due to HCN volatilization.

The analytical method found most suitable for the determination of cyanide concentrations was the picric acid colorimetric method [8, 9]. The procedure involved adjustment of the pH of a 10 ml sample to a slightly basic value, addition of 5 ml of a 1% aqueous solution of picric acid and 5 ml of a 0.5 *M* aqueous solution of Na_2CO_3 , heating in a boiling water bath, cooling back to room temperature and measuring the absorbance at 520 nm against a reagent blank. The method was found to be applicable to TCLP leachates containing cyanide as well as to the determination of cyanide in solid carbon samples following extraction of the cyanide by means of distillation from a sulfuric acid medium and absorption of the vapors in 1.25 *M* NaOH [10]. The picric acid method was found to have a linear range of at least 50 mg/l CN^- and a detection limit of 0.2 mg/l CN^- .

The analytical method found most suitable for the determination of fluoride concentrations was the use of a fluoride electrode [11–13]. The procedure involved dilution of a 5 ml sample to 50 ml with a 15% aqueous solution of CH_3COONa and the addition of a 5 ml CDTA-based buffer (Orion Research TISAB III) followed by measurement of the potential by means of a fluoride combination electrode with a linear range of at least 100 mg/l F^- . The CDTA buffer was added in order to break up metal fluoride complexes and thus ensure that all the fluoride in the leachates was analyzed. The fluoride content of solid spent carbon was determined using the same method following ashing according to Remmert's method [8] and distillation of the ashed sample from a sulfuric acid solution [11].

3. Results

3.1. Characterization of spent liner material

Analysis of spent liner material from two industrial sources showed that in one case the fluoride concentration in the carbon was 7.6% and the cyanide concentration 0.18%, and in the other case the fluoride concentration was 9.8% and the cyanide concentration <0.01%. In the case of the first material, the TCLP leachates contained (1500 ± 90) mg/l F^- and 2.6 mg/l CN^- , while the leachates of the second material contained (2230 ± 20) mg/l F^- and <0.1 mg/l CN^- . The large difference in cyanide concentrations is likely to be due to differences in electrolytic cell technology among various manufacturers, as well as differences in the location from which the liner sample came inside the electrolytic cell. In general, the variability in cyanide concentrations within a cell is large, as is the variability in this respect among individual cells and among different types of cells. Based on the concentrations given above, all the work on cyanide removal was performed on the first batch of carbon. Most of the fluoride studies were carried out on the second batch of carbon.

3.2. Cyanide removal

The chemical cleaning method used to remove the cyanide contamination was based on the use of NaOCl, which is known to oxidize CN^- to OCN^- ,

Table 1

Results of TCLP tests on spent liner material stirred with various aqueous media, 1 g carbon samples, 40 ml solution volume, 16 h and room temperature

Cleaning solution	F ⁻ concentration in TCLP leachates (mg/l)		
	1st TCLP	2nd TCLP	3rd TCLP
None	2230		
TISAB III CDTA buffer ^a	731		
TISAB II CDTA buffer ^a	720		
0.1 M CH ₃ COOH	605		
Deionized water	466		
1 M NaOH	302		
1 M HCl	236		
1 M LaCl ₃	426	157	101
1 M MgCl ₂	314	161	127
1 M Ca(OCl) ₂	228	167	119
1 M CaCl ₂	227	154	118
NaOCl (5% available Cl)	220	98	65
1 M ZrOCl ₂	99	25	63

^a Orion Research, Cambridge, MA.

followed by decomposition of the OCN⁻ into NH₃ and CO₂. The rate of this process is pH dependent, and is lowest in strongly alkaline solutions [14,15]. The chemical cleaning technique which was tested consisted of stirring 1 g of spent liner material, in the form of a few chunks (each several mm in size), in 100 ml of a solution of NaOCl having a 2.5% available chlorine content and adjusted with HCl to a desired pH in the range 6–10, for a period of 5 h at room temperature. Solutions with pH values lower than 6 were not used in order to avoid the possibility of HCN volatilization. In two different experiments at pH 10 on carbon containing 0.18% CN⁻, the cyanide content was found to drop by 88% and 85%, respectively. These percentages represent the decrease in the cyanide content of the solid carbon material analyzed according to the procedure described in the experimental part (sulfuric acid distillation [10] followed by absorption in alkali and picric acid colorimetry). At pH 8 the drop was by 91 and >97%, respectively. At pH 6.5 the cyanide content decreased by 97% in both cases. It was concluded that chemical cleaning with a solution of NaOCl in the pH range of 6–8 is a very effective means of eliminating cyanide contamination from spent carbon material.

3.3. Fluoride removal

Unlike cyanide, fluoride present in the spent liner material cannot be destroyed by oxidation in aqueous solution. Because the fluoride problem is more intractable, most of the experimental work was aimed at attempting to remove the fluoride impurity by extraction with aqueous media differing from one another in pH and ionic composition.

The first set of experiments was carried out by stirring together 1 g of spent carbon with 40 ml of each of a series of leachants for 16 h at room temperature. Afterwards, the carbon was filtered out and subjected to a TCLP test. In certain cases, three consecutive TCLP tests were carried out on the treated carbon. The results of this set of experiments are summarized in Table 1.

The results suggest that strongly acidic or basic solutions are more effective in cleaning carbon than weak acids or water. The effectiveness of each treatment under the conditions of time, temperature and volume:weight ratio used in the experiments is limited to the removal of fluoride present close to the surface of the carbon, as shown by the fact that further TCLP tests on the same samples yield values which are much less dependent on leachant composition than those obtained in the first test. As indicated by the third TCLP values, this is true even in the case of ZrOCl_2 , which appears to be the most effective solute.

The use of concentrated salt solutions is expensive and is likely to complicate the removal of fluoride from the leachant for further reuse. Accordingly, subsequent tests concentrated on the use of common acids and bases and explored the possibility of enhancing the effectiveness of fluoride removal by increasing the time, temperature, and volume:weight ratio. End-over-end rotation of the treatment flask (using the TCLP rotator) was substituted for simple stirring. The results of the second set of experiments are given in Table 2.

The results shown in Table 2 confirm the observation that strong acids (or bases) are more effective in removing F^- from the carbon than weak acids or water. For practical purposes, it is important to note that acid solutions prepared using tap water are as effective as those prepared with deionized water. While the results in Tables 1 and 2 indicate that the effectiveness of the solutions of certain salts (especially ZrOCl_2) in removing fluoride is comparable to the effectiveness of strong acid solutions, acid solutions have the advantages of lower cost and of avoiding complications which may arise from the deposition of salt residues inside the washed liner material.

Table 2

Results of TCLP tests on spent liner material agitated with various aqueous media, 1 g carbon samples, 64 h and room temperature

Cleaning solution	Solution volume (ml)	F^- concentration in TCLP leachates (mg/l)
None		2230
Deionized water	1000	310
1 M NaOH	1000	99
1 M HCl	1000	63
0.1 M CH_3COOH	1000	191
1 M NaOH	2000	66
1 M HCl	2000	60
1 M HCl^a	2000	57
0.5 M H_2SO_4^a	2000	57

^a Acid solution prepared using tap water; all other solutions made up in deionized water.

Table 3

Results of TCLP tests on spent liner material agitated with multiple volumes of various aqueous media, 1 g carbon samples

Cleaning solution	Temperature (°C)	No. of volumes	Time (h)	Solution volume (ml) (each portion)	[F ⁻] in TCLP leachates (mg/l)
None					2230
0.5 M H ₂ SO ₄	RT	2	4+17	500	115
0.5 M H ₂ SO ₄ ^a	RT	2	4+17	500	116
0.5 M H ₂ SO ₄	RT	3	2*3.5+16	500	47
0.5 M H ₂ SO ₄	RT	2	4+16	750	49
0.5 M H ₂ SO ₄	RT	5	5*0.5	750	205
	RT	+5 ^b	5*0.5	750	174
0.5 M H ₂ SO ₄	83.4 °C	5	5*0.5	750	83
	77.3 °C	+5 ^b	5*0.5	750	74

^a Acid solution prepared using tap water; all other solutions made up in deionized water.

^b Additional treatments of carbon following the five treatments listed on previous line.

The experiments described so far were all performed by agitating the solid carbon with a single volume of leachant. The next set of experiments was designed to examine the effects of using several volumes of fresh leachant one after the other while attempting to reduce the treatment time. Experiments were carried out at room temperature as well as around 80 °C. The method of agitation was end-over-end rotation as in Table 2. The results are summarized in Table 3. Table 3 denotes the number, volume and time of each of the individual washes used in each multiple treatment experiment. For instance, the terminology '2 × 3.5 + 16 h, 500 ml' means that the 1 g carbon sample was washed twice, each time for 3.5 h, followed by a single wash for 16 h, and that the volume of the wash solution employed in each of the three operations was 500 ml.

The results listed in Table 3 again show that the substitution of tap water for deionized water in preparing the H₂SO₄ solution for cleaning the carbon does not affect the results. Cleaning the carbon with 1500 ml/g of acid over a period of (21 ± 2) h gives the same results whether two or three volumes are used, indicating that total volume and time control the effectiveness of the treatment. Finally, the results show that an increase in temperature is very beneficial.

In view of the large volumes of acid used in effective cleaning of the spent liner material, removal of extracted fluoride from the acid so that this acid can be further used may greatly improve the economics of the chemical cleaning process. Accordingly, it was attempted to remove fluoride from some of the 0.5 M H₂SO₄ solutions previously used in the experiments listed in Tables 2 and 3 by passing these solutions through beds of sorbent. Among the various sorbents used to remove F⁻ from aqueous solutions [16, 17], activated alumina has been used as a choice in removing fluoride from neutral aqueous media [18, 19] while charcoal has its optimum capacity for F⁻ removal around pH 3 [20–22]. The columns used had a volume of 50 ml and a height of 50 mm. The rate of flow was 10 ml/min, corresponding to a residence time of 5 min. The results of the column experiments are shown in Table 4.

Table 4

Removal of fluoride from spent 1 M H₂SO₄ cleaning solutions using adsorbents, 5 min residence time and room temperature

F ⁻ concentration (mg/l, initial)	Column material ^a	F ⁻ concentration (mg/l, final)	F ⁻ removal (%)
51	Alumina A	16	68
51	Alumina B	11	79
30	Alumina A	7	76
30	Alumina B	6	81
142	Alumina A	51	64
142	Alumina B	34	76
43	Alumina A	17	61
43	Alumina B	13	70
31	Alumina A	10	67 ^b
31	Alumina B	10	68 ^b
31	Alumina C	6	79 ^b
31	Charcoal	28	10 ^b

^a Alumina A = activated Al₂O₃, -8 + 14 mesh, Fisher Scientific; Alumina B = adsorption Al₂O₃, -80 + 200 mesh, Fisher Scientific; Alumina C = neutral Al₂O₃, chromatography grade, -100 + 200 mesh, Fisher Scientific; Charcoal = activated carbon, -80 + 200 mesh, Fisher Scientific.

^b Average of five individual column runs.

The results show that alumina is much more effective than charcoal in removing fluoride from spent sulfuric acid cleaning solutions, as may be expected because charcoal is generally ineffective in removing significant amounts of simple anions from solution. The results also show that there are no large differences in effectiveness among the three varieties of porous alumina used in the present study.

4. Discussion

The studies reported here show that cyanide and fluoride, the hazardous constituents present in spent liner material from electrolysis cells used in aluminum production, can be effectively removed by chemical cleaning. In the case of cyanide, treatment with NaOCl (2.5% available chlorine solution, pH 6.5) for 5 h results in a destruction of >97% of the total cyanide content throughout the entire mass of the sample. Treatment with 0.5 M H₂SO₄ for about 21 h at room temperature can reduce the amount of leachable fluoride by almost 98%, while a reduction by more than 96% is obtained in 2.5 h at a temperature of 80 °C. The studies also show that about 80% of the fluoride extracted from the spent liner into 0.5 M H₂SO₄ can be removed by passing the acid through an alumina bed at a flow rate of 0.2 bed volumes/min.

The results obtained in the present study show that the chemical cleaning is a potentially useful technique for removing cyanide and fluoride from spent liner material, making it possible to dispose of the material as non-hazardous or to reuse it. Although fluoride removal requires a substantial volume of acid, this acid can be

used again after removing most of the fluoride by passing the solution through a bed of alumina. Indeed, although the results presented here do not indicate that solution exchange results in large savings in time as long as the total volume of leachant remains unchanged, it may be most convenient to carry out the chemical cleaning operation in flow mode rather than in batch mode. In this case, the acid solution will be continuously pumped through the vessel containing spent liner material, then passed through an alumina bed, and then brought again in contact with spent liner material. Carrying out the chemical cleaning operation at elevated temperature can result in considerable savings in time.

Eventually, the capacity of the alumina bed used to remove fluoride from the spent cleaning solution will be exhausted. The fluoride-loaded alumina can thereupon be added to the alumina/cryolite feed of the electrolytic cell, thus avoiding the generation of secondary wastes. Alternatively, the alumina bed may be regenerated using inexpensive reagents such as NaOH [23, 24] or alum [25]. The dissolution of alumina in dilute sulfuric acid at ambient temperature is extremely slow [26, 27], and recycling the acid will minimize the necessity to dispose of the aluminum-contaminated leachant.

Chemical cleaning is likely to be effective in treatment of spent liner material on a larger scale, since the used carbon contains a multitude of cracks and fissures, where the impurities in the carbon are concentrated. Accordingly, the laboratory scale experiments described above provide a realistic basis for upscaling the process and providing a route for minimizing the volume of hazardous waste generated by the aluminum industry.

It should be emphasized that the work described here was carried out on carbon from only two sources, one used in the cyanide studies and the other in the fluoride studies. Future work should include studies with anthracite carbon from a larger variety of sources (origin of carbon, liner production procedure, and, in particular, type of electrolytic cell and location of the liner sample in the electrolytic cell). The development of an effective and economically feasible washing technique to remove the bulk of the contaminants from the spent liner material may broaden the range of applications for reusing this material and alleviate the problem of dealing with this material as hazardous waste.

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References

- [1] K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky and J. Thonstad, *Aluminum Electrolysis: Fundamentals of the Hall–Heroult Process*, Aluminum-Verlag, Duesseldorf, Germany, 2nd edn., 1982.

- [2] P. Brilloit, L.P. Lossius and H.A. Øye, *Metall. Mater. Trans. B* 24B, (1993) 75.
- [3] C. Allaire and P. Desclaux, *Metall. Mater. Trans. B*, 25B (1994) 221.
- [4] United States Environmental Protection Agency, "Method 1311: Toxicity Characteristic Leaching Procedure", Code of Federal Regulations, Title 40, Chap. I, Part 261, Appendix II, 7-1-90 Edition, Government Printing Office, Washington, DC, p. 64.
- [5] C.-H. Lee, H.-C. Wang, C.-M. Lin and G.C.C. Yang, *J. Hazard. Mater.*, 38 (1994) 65.
- [6] W.S. Rickman, *Light Met.*, (1988) 735.
- [7] L.C. Blayden, S.C. Hohman and S.J. Robuck, *Light Met.*, (1987) 663.
- [8] D.F. Boltz and J.A. Howell, *Colorimetric Determination of Nonmetals*, Wiley, New York, 2nd edn., 1978.
- [9] H.B. Singh, N. Wasi and M.C. Mehra, *Int. J. Environ. Anal. Chem.*, 26 (1986) 124.
- [10] United States Environmental Protection Agency, "Method 9010: Total and Amenable Cyanide", 1st Revision, EPA, Washington, DC, 1987.
- [11] American Public Health Association, *Methods of Examination of Water and Wastewater*, 12th edn., American Public Health Association, Washington, DC, 1985.
- [12] M.S. Frant and J.W. Ross Jr., *Science*, 154 (1966) 1553.
- [13] J. Pavel, R. Kuebler and H. Wagner, *Microchem. J.*, 15 (1970) 192.
- [14] W.M. Lister, *Can. J. Chem.*, 33 (1955) 426.
- [15] C.M. Gerritsen and D.W. Margerum, *Inorg. Chem.* 29 (1990) 2757.
- [16] J.A. Harmon and S.G. Kalichman, *J. Am. Water Works Assoc.*, 57 (1965) 245.
- [17] W.-W. Choi and K.Y. Chen, *J. Am. Water Works Assoc.*, 71 (1979) 562.
- [18] C.S. Boruff, *Ind. Eng. Chem.*, 26 (1934) 69.
- [19] S. Meenakhshi, A. Pius, G. Karthikeyan and B.V.A. Rao, *Indian J. Environ. Prot.*, 11 (1991) 511.
- [20] R.H. McKee and W.S. Johnston, *Ind. Eng. Chem.*, 26 (1934) 849.
- [21] W. Balinski, *Gas, Wasser, Waerme*, 31 (1977) 256.
- [22] D.S. Bhargava and S.D.J. Killedar, *Res. J. Water Pollut. Control Fed.*, 63 (1991) 848.
- [23] G.J. Fink and F.K. Lindsay, *Ind. Eng. Chem.*, 28 (1936) 947.
- [24] K.V. Rao and C.L. Mahajan, *Hazard. Ind. Waste*, 20 (1988) 55.
- [25] A. Savinelli and A.P. Black, *J. Am. Water Works Assoc.*, 50 (1958) 33.
- [26] A. Mitscherlich, *J. prakt. Chem.*, 81 (1860) 110.
- [27] M.D. Crawford, J. Baumgart, M. Shoaie and W.R. Ernst, *A.I.Ch.E. J.*, 34 (1988) 2012.