Recycling Possibilities of Spent Potlining Carbon Material Generated from NALCO's Smelter

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Abstract

Total 6 000–7 000 tonnes of Spent Potlining Material (SPL) is generated from aluminum electrolysis process of NALCO's smelter each year, out of which around 45–50 % is carbon portion (first cut) and rest is refractory portion along with other insulating lining materials. SPL has been classified as hazardous waste by Indian environmental regulations due to the presence of mainly leachable fluoride and cyanide constituents. Safe disposal of this unavoidable but hazardous waste product is a challenge faced by NALCO. This paper focuses on laboratory scale investigation on SPL carbon portion (first cut) for finding its recycling possibilities after treatment. The major constituents of SPL carbon portion (first cut) are carbon, fluorides, sodium compounds, along with minimum amount of sodium cyanides and other impurities. The basic process involves pressure leaching of ground SPL in water to remove cyanides, recovery of sodium as sodium hydroxide solution, recovery of fluorides as calcium fluoride and possible utilization of treated carbon in prebaked anode matrix.

Key words: Spent pot lining, Pressure leaching, Recovery of fluorides and carbon, Prebaked anode.

1. Introduction

In the Hall-Héroult smelting process, aluminum oxide is dissolved at 960 °C in a molten electrolyte composed of cryolite, aluminium fluoride, calcium fluoride, and some other minor compounds; dissolved alumina is electrolyzed to give aluminum metal at the cathode and oxygen gas at the anode [1].

In the aluminium production pot, the electrolyte and the molten aluminium are contained in a steel shell lined with refractory and thermally insulating material at the bottom and carbon cathodes and side slabs sealed with ramming paste at the upper layer of pot lining. Graphitic, graphitized or semi-graphitized materials are now used extensively as prebaked carbon cathode blocks. The other materials used are semi-graphite and silicon carbide (SiC) sidewall bricks and carbonaceous ramming paste. Steel collector bars are embedded in the carbon cathode to conduct the electric current away from the pot. Figure 1 shows a schematic drawing of an aluminium electrolysis pot.

Insulation bricks and refractory bricks are used to insulate the cathode thermally. These bricks are porous and vulnerable to penetration of electrolyte components through the cathode blocks. The real acting cathode from an electrochemical point of view is the top surface of the molten aluminum pool.

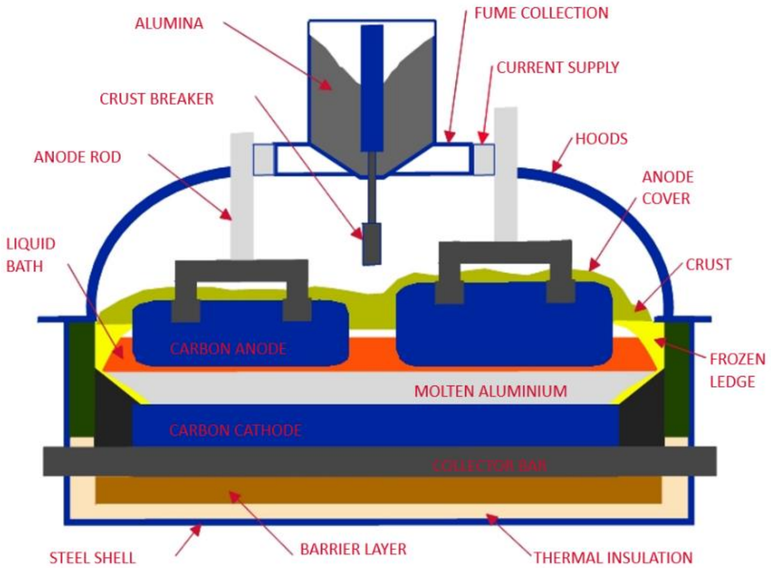

Figure 1. Schematic drawing of an aluminum electrolysis pot.

Pots are now typically 9–18 m long, 3–5 m wide, and 1–1.5 m deep. The depth of the operating pot cavity is relatively low, about 0.4–0.6 m. Carbon is the material chosen to withstand best the combined corrosive action of molten fluorides and molten aluminium. However, in actual operation, the frozen electrolyte protects the sides of the pot. Nowadays silicon carbide is used as sidewall material, but this material is also corroded by the electrolyte and needs to be protected.

The pot is shut down when the damage to the cathode does not allow it to continue its operation, usually after a period of 5–10 years. The material generated after removing bath material and aluminum metal and separating cathode bars is called spent pot lining, comprising carbon materials (first cut) originating from the cathode blocks, side blocks and lining paste and the refractory and insulating materials (second cut).

The spent lining material, which is composed of carbon, refractory material and cryolite, including fluorine, aluminum, sodium, calcium and silicon values, along with free and complexed cyanides, carbides and nitrides, is hazardous due to leachable fluorides and cyanides and must be treated safely. The safe disposal of spent linings has for a long time presented a challenge to the industry. That challenge continues with ever stricter environmental standards. Thus, disposal residues are limited to very low concentrations of fluorides and cyanides.

There is no global sustainable solution for management of SPL. The disposal and treatment practices adopted for SPL is highly diversified, ranging from sea deposits, secured landfill to dedicated plant and region specific valorization plants. SPL treatment costs vary widely and they mainly depend on the type of process and product use or reuse and regional regulations.

As per reports, few aluminum companies in India and abroad have started recycling SPL in cement industries and steel industries, third party alternatives exist to treat SPL [2].

There are two general categories of technology, i.e., technology that treats and stabilizes the waste (rendering the waste harmless) and enables landfilling of the stabilized-waste, and technology that focuses on making products out of the waste. There are hydrometallurgical and pyro metallurgical options for both categories.

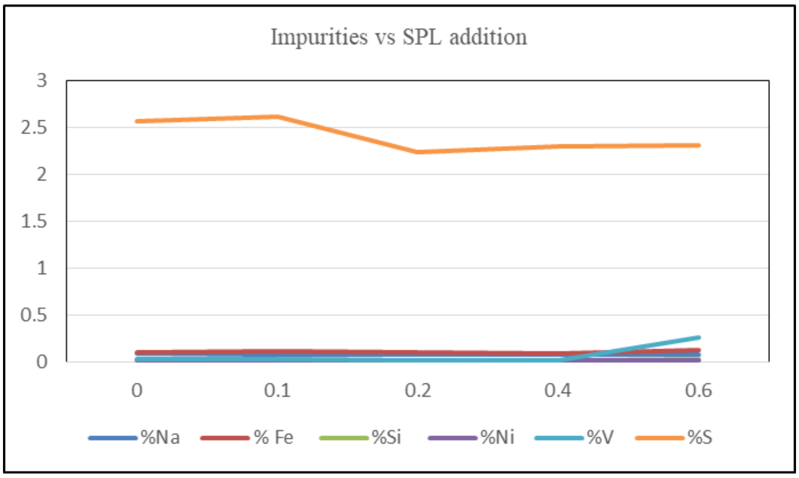

Figure 13. Anode impurities vs SPL carbon addition.

Observation: Influence of SPL Carbon (after pressure leaching) additions on anode density is shown in Figure 10, on reactivity behavior is shown in Figure 11 and on impurities is shown in Figure 12.The results of the above experiment show that minimal quantity of SPL carbon can be safely added into green anode recipe without affecting the quality of prebaked anodes. If 0.5 % SPL carbon is added to the anode recipe the quantity of SPL carbon that can be recycled per year in NALCO's smelter plant would be around 1500 t out of 2500-3000 t generated.

5. On-Going Work and Future Plan

i. Development of the process in 50-100 kg capacity and further optimization of leaching conditions, liquor recycling, fluoride recovery, NaOH quality, water balancing.
ii. Flow sheet development and pilot plant trial.
iii. Generation of sufficient quantity of material for validation of results in the plant.
iv. Large scale plant trial in limited pots with anodes made by addition of around 0.5 % SPL carbon obtained after leaching.

6. Conclusions

i. The composition of spent potlining material is widely variable depending on age of pots, digging procedure, storage and sampling.
ii. Preliminary lab scale studies conducted in the above study at NALCO show that it is feasible to reuse the carbon recovered from SPL carbon portion in pre baked anode recipe. The quantity to be recycled will depend on the % Na and % F in the material.
iii. The alkali extracted from the process can be recycled into the Bayer process after increasing its concentration.
iv. The non-hazardous calcium fluoride precipitated from the liquor can be sold to outside parties or can be disposed-off in cement plants.

7. References

1. Kai Grjotheim, *Aluminium Electrolysis,* Aluminium Verlag 1983.
2. Stephan Broek and Harald Arnljot Oye, Fundamentals of managing spent potlining, *Proceedings of the 36th International ICSOBA Conference*, Brazil, 29 October- 1 November 2018, *Travaux* 47, 817-833.
3. Morten Sørlie, Harald A. Øye, *Cathodes in aluminium electrolysis*, 3rd Edition, Aluminium Verlag 2010.

4. Rudolf P. Pawlek, Spent potlining: water soluble components, landfill and alternative solutions, *Light Metals* 1993, 399-405.
5. Frank M. Kinmerle et al., Cyanide destruction in spent potlining, *Light Metals* 1989, 387-394.
6. G.A. Wellwood and, D. P. Rodda, Utilisation of fluoride and Na value from calcined spent potlining, *Light Metals* 1994, 261-267.
7. Harald Øye, Discussion of industrial spent potlining treatment, *Proceedings of 35th International ICSOBA Conference*, 2-5 October 2017, Hamburg, Germany, 2017, Travaux 46, 1081-1088.
8. *Anodes for Aluminium Industry*, R&D Carbon Ltd, Switzerland.