## **Conceptual Design of a Commercial Spent Pot Liner Treatment Plant.**

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**ABSTRACT:** All aluminium smelter plants discharges high volume extremely toxic electrolytic cell waste known as spent pot liner. Over the years scientists have improvised various methods for disposing these toxic wastes either by diluting with inert material or recovering its carbon value after decontaminating the toxic waste. Present paper outlines conceptual design of a commercial treatment plant which allows recovery of its carbon value. The design is based on long experience of the authors in decontaminating SPL and recovering its carbon value.

### I. INTRODUCTION:

Aluminium smelter plants use age old Hall Heroult electrolysis method for extracting aluminium metal from molten cryolite in a thickly carbon lined steel vessel where the carbon lining serves as cathode of the cell. The molten salt containing fluoride which ultimately corrodes these carbon lining(pot liner) and results in failure the cell when they are rejected as toxic carbon waste known as spent pot liner or SPL in short. The toxic waste besides being highly voluminous, its disposal is a challenge to plant engineers and scientist for a very long time. One method currently being pursued in USA involves diluting the waste with inert materials (like sand and lime) and use them as landfill. But the process is costly and adds to the cost of production of the metal. Mazumder et al<sup>1-3</sup> at IIMT, Bhubaneswar, India evolved a process whereby the SPL is crushed to about 4-6 mm size and treated with strong acids resulting in complete removal of the contaminants and recovery its carbon value.

It may be mentioned here that SPL contains several toxic contaminants (shown in Table 1 below) and the carbon recovered from such wastes are generally semi crystalline in nature.

#### Table 1: Contaminants in spent pot liner

Contaminants	Typical range (%)
Alkali	11-20
Aluminium	5-10
Fluoride	5-20
Cyanide	0.12-0.20

Pilot plant trial (1 ton SPL/day) for decontaminating SPL by above acid treatment procedure by Mazumder et al. was highly successful and brought down all above toxic contaminants to its acceptable limits. However, cost of production of recovered byproduct carbon by this process was still high for making any industrial carbon products from these recovered carbon economically feasible. Microscopic studies of SPL boulders (as it comes out from production plant) indicates most of the toxic contaminants remains as a thin layer on surface of SPL boulders or diffuse into it through its fine cracks. Based on these informations, present authors improvised experiments for treating large boulders of SPL (first cut only) without powdering them, as was done earlier and the results are shown below.

### II. EXPERIMENTAL:

Boulders for present experiments were handpicked from the piles of first cut SPL from the aluminium smelter plant. Fluoride in SPL before and after treatment was determined using Ion Selective Electrode . The procedure involves weighing out a sample of 100 mg into a 10 ml platinum crucible and mixing the same with 0.5 gm of anhydrous sodium-carbonate and 0.1 gm of zinc oxide. The mixture is then heated to 900  $^{0}$ C for 30 minutes. After cooling the crucible is placed into a 50 ml borosilicate glass beaker, to which 30 ml of water was added and the beaker was covered and digested overnight at steam bath temperature. The crucible is then washed, any lump present is broken, and the solution is allowed to cool to room temperature.

The contents are then filtered into a 100 ml volumetric flask using No.42 Whatman filter paper (or its equivalent), and the residue is washed several times with small portion of a 0.1 % sodium-carbonate solution. The residue thus obtained is rejected. Then 2 ml of 6N Hydrochloric acid is added slowly to the solution, shaking vigorously to expel the carbon-dioxide, and diluted to volume with water. Diluted a 45 ml of aliquot of this solution with 5 ml TISAB solution, and measured the potential of the diluted solution by Ion Selective Electrode.

#### Measurement of potential:

a) A series of minimum 3 standards were prepared with the same back ground ionic strength (which can be done by adding the same volume of TISAB to all the standards i.e 19, 190,1900 ppm) bracketing the sample fluoride concentration.

b) The Ion Analyser was then calibrated by feeding the standards, starting from dilute to a concentrated standard.

c) Same volume of TISAB was added to the sample as that of standards and then feed the sample whose concentration can be directly read with the Ion Analys

Make: ELICO Ion Analyzer. Model No. LI 126.

A strong oxidizing acid was used to remove fluoride from SPL. SPL when comes in contact with strong oxidizing agent raises temperature of the solution high enough to break down  $CN^-$  present in it. The vessel used for dipping the boulders in the oxidizing acid was glass lined and enough acid was taken to ensure complete dipping of boulder into the acid. Boulders were dipped into the acid for 5 minute, 15 minute, 30 minute, 1 hour and 2 hours. After each specified period, the boulder was taken out of the acid, thoroughly washed with distilled water and dried before determining their fluoride content. The dried boulder was powdered to -100 BS mesh size and representative sample was taken out of the heap by quarter and coning method.

Results of the experiments on shown in Table-2 below:

		Fluoride content after
Size of the SPL boulder	Initial F content	5min 15min 30min 1hr 2hrs
8.5 kg	2.4 %	12 ppm 7 ppm 7 ppm 7 ppm 7 ppm
9.66 kg	2.7 %	14 ppm 8 ppm 8 ppm 8 ppm 8 ppm
13.65 kg	2.8 %	14 ppm 8 ppm 8 ppm 8 ppm 7 ppm
15 kg	2.8 %	15 ppm 10 ppm 9 ppm 9 ppm 8 ppm

Table 2: Removal of fluoride from SPL boulder	with time
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It is obvious from above table that essentially all fluoride is removed from SPL boulders by such acid treatment in about 15-20 minutes reaction time. Accordingly design of a commercial plant is envisaged, as elaborated below, for decontaminating SPL boulders as they come out from aluminium smelter plant.

#### Design of a commercial unit;

Since the strong oxidizing acid used in these experiments react with most common metals and it is difficult to handle large glass vessels in commercial scale, a SS 317 vessel was found suitable as material of construction of reaction vessel for the commercial plant. Treatment of SPL boulders by above methods has an added advantage over powdering and treating the powdered raw material. First the reaction does not emanate high heat in very short time, gives out less smoke from the treatment tank, and since the treated product is large in size does not cause high pressure drop in the filter system. Additionally the treated product has less ash in it.Fig.1 below shows schematic diagram of the entire plant. First the boulders are dipped into acid kept in a large steel tank which has got arrangement for draining out the reacted acid and empting the reacted boulders on a conveyer belt (made of glass fiber) which ultimately empties the reacted boulders in a water washing tank. After washing, the SPL boulders are dried in an oven at about 110 °C and then powdered in a jaw crusher cum hammer mill to desired size. Reacted acid can then be taken out of the reaction vessel into a holding tank and reused for further reaction with next batch of SPL bolders. Spent acid thus can be reused several times until its strength goes down to a certain level. Preliminary experiments by the present author have indicated that the spent acid can be re-used 6-7 times before it is being discarded, thus bringing down the acid treatment cost substantially by this process. By product carbon thus obtained has multiple use in producing useful industrial carbon products<sup>4-10</sup>. As a measure of safety since the process uses very strong acids, the plant (particularly each section or unit operation) needs to be covered by transparent acrylic sheets and all the operation needs to be carried out remotely. Toxic gases from the plant needs to be removed by appropriate exhaust form and bubbled through caustic lime solution before venting out to atmosphere. Attempts may be made to recover fluoride from the spent acid and returned to the plant as aluminium fluoride. Similarly washed water from the plant needs to be recirculated and spent water neutralized with lime before it is discharge to the open drain.

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