Recycling of Solid Wastes in Aluminum Electrolysis in China

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Abstract

Solid wastes from primary aluminum smelter include spent pot linings after pot failure, carbon dust and spent electrolyte generated during pot operation. In this paper a critical review on recycling techniques of solid waste developed by Chinese smelters is given, especially on the recycling techniques of spent cathode blocks. We think the future emphasis should be on the development of green recycling techniques for spent cathode blocks in Chinese smelters. Green technology should change spent cathode blocks from the present harmful waste to a useful resource.

Keywords: Aluminum electrolysis, solid waste, recycling, green technology.

1. Introduction

In 2018, China produced 36.485 million tonnes of primary aluminum [1]. Most of it is produced by high amperage cells of 300 kA and higher. The cells must be shut down after five to eight years because of pot failures, caused by penetration of electrolyte to the refractories, cathode block erosion and corrosion attack of iron collector bars by liquid aluminum. The spent pot linings (SPL), including spent carbon blocks, spent refractories and spent insulation materials must be changed to harmless materials. According to our estimation, the total amount of spent carbon blocks is about 300 kt per year in China. The total generation amount of SPL per tonne of aluminum produced is 30 - 50 kg, corresponding to generation of at least 1 million tonnes of SPL per year in China.

Besides SPL, carbon dust and spent electrolyte generated during pot operation are the other two kinds of solid wastes. As we know, electrolysis cell always generates electrolyte according to Equation (1). The electrolyte generated in this way can be used to start up new cells and as covering material for anode. However, after the startup of a new potlines, smelters do not need so much electrolyte, consequently, the new generated electrolyte must be recycled in the future. At present, many Chinese smelters store a large amount of spent electrolyte, which will need to be treated properly in the future. In some smelters, whose spent electrolyte contains high content of lithium and potassium, the situation is more serious.

$$4AlF_3 + 3Na_2O = Al_2O_3 + 2Na_3AlF_6 \quad (1)$$

2. Recycling of Spent Potlining.

In China, the main purpose of SPL treatment is to change it to harmless materials which meet the standards of Chinese Environmental Regulations. Some new technologies have been developed to change solid wastes to reusable raw materials, which might attract more enterprises to devote to the recycling of solid waste generated in aluminum industry.

All methods can be divided into two categories: pyro-process and hydro-process. Some methods have been commercialized in China.

2.1 Flotation Process

In 1989, Prof. Qiu Zhuxian and Dr. Zhai Xiujing firstly began to separate electrolyte from carbon in SPL by flotation method [2]. In 1989, the primary aluminum production capacity was less than 1 million tons in China.

In 1993, some industrial tests of flotation process for SPL were conducted in Fushun Aluminum Smelter, Qingtongxia Aluminum Smelter and Guangxi Pingguo Aluminum Smelter [3].

From 2007 - 2010, with the support from the National Development and Reform Commission of China, Northeastern University cooperated with Yichuan Electric Power Co. Ltd to commercialize the flotation process. A pilot plant with a processing capacity of 3000 tons/year was built. The operation confirmed that the average carbon content of recycled carbon powder was in the range of 85 – 90 %, the purity of electrolyte was approximately 90 %, containing about 5 % carbon.

2.2 Alkaline-Acid Leaching Process.

The process of Alkaline-Acid Leaching (AAL) to recycle the SPL is proposed by prof. Zhongning Shi in Northeastern University [4]. The principle of the process is based on the Equations (2) to (3) in alkaline leaching and Equations (4) to (6) in acid leaching.

$$Na_3AlF_6 + 4NaOH \rightarrow NaAl(OH)_4 + 6NaF \quad (2)$$

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4 \quad (3)$$

After alkaline leaching, the carbon content in carbon block increases from 65 % to 73 %. The main impurities, $NaAl_{11}O_{17}$ and CaF_2 can be further removed by acid leaching according to reactions 4 to 5. Finally, the purity of recycled carbon powder can reach up to 97 %, which can be used as raw material for anode production.

$$NaAl_{11}O_{17} + 34HCl \rightarrow NaCl + 11AlCl_3 + 17H_2O \quad (4)$$

$$CaF_2 + 2HCl \rightarrow CaCl_2 + 2HF \quad (5)$$

$$NaOH + HCl \rightarrow NaCl + H_2O \quad (6)$$

2.3 Vacuum Distillation Process

In 2015, Professor Feng Naixiang invented a new method for treatment and recycling of spent potlining [5 - 6]. Spent carbon materials, including spent pot-lining and carbon dust, are heated in a vacuum furnace at 1000 to 1400 °C. The volatile materials including sodium metal and fluorides are then separated from the carbon. Because of the melting point difference, sodium metal will be solidified at temperatures below 500 °C, and the electrolyte in the range of temperatures 500 to 1000 °C in the upper part of the vacuum chamber. After such treatment, the purity of carbon can reach up to 92 % and higher. The new method can also be used to recycle the spent insulating

materials by addition of aluminum dust from the foundry shop. Aluminum reacts with sodium oxide to produce metallic sodium. During the step of distillation cryolite-based electrolyte and metallic sodium are removed from the insulating materials, which can be used again in prebake cells.

2.4 CHALCO SPL Process

In 2003, CHALCO developed a pyro-process for treatment of SPL. Mixture of SPL, lime and coal flying ash is baked in the rotary furnace at 900 to 1100 °C. The fluoride vapor is absorbed by alumina in the dry scrubbing system to recycle fluorides; solid remains, mainly CaF_2, are sent to cement factory as raw materials.

Up to 2017, two industrial treatment lines of SPL based on CHALCO-SPL process [7] were put into operation successfully. The latest line has treatment capacity of 10 000 tons per year and produces raw materials for cement manufacture.

3. Recycling of Spent Electrolyte

In China, alumina with high content of Li_2O and K_2O is used to compensate the great demand for alumina in Chinese aluminum smelters because of the rapid expansion of primary aluminum production capacity in China. These impurities react with aluminum fluoride to form corresponding fluorides, LiF and KF. Both lithium and potassium gradually enrich in the aluminum electrolyte and reach a high level in a few years [8]. Even though additives like KF and LiF might benefit the electrolysis process by lowering the liquidus temperature of the electrolyte, they cause several operation troubles to the reduction cell at the same time. At present, aluminum electrolytes containing 3 % LiF and 2 % KF are very common in most Chinese smelters who use the above alumina. In the worst case, the bath contains 7 % LiF and 4 % KF, which cause poor dissolution behavior of alumina in aluminum bath and unstable electrolysis cells [9]. In general, the excess electrolyte generated according to Equation (1) must be tapped from the cell and can be used to adjust the bath level of other cells or used to start new cells. Some solid electrolyte can also be used for anode cover materials. However, if the electrolyte containing high contents of LiF and KF is kept in the bath recycling, the electrolyte of other cells will be polluted, and the increasing trend of lithium and potassium in electrolyte cannot be inhibited. Therefore, it is very important to find some solutions to decrease the lithium and potassium contents in the aluminum bath. In China, the spent electrolyte with high content of LiF and KF must be removed from the bath recycling and stored without treatment in smelters. It is estimated that China produces about 500 000 tonnes of spent electrolyte of this kind per year.

Northeastern University developed two methods to recycle the spent electrolyte: acid leaching [10 - 16] and aluminum salt leaching [17]. In the acid leaching method, lithium is separated from cryolite and transformed to lithium carbonate. HNO_3, H_2SO_4 and HCl were tried to dissolve the lithium compounds in solid aluminum electrolyte, respectively. HNO_3 exhibits the highest leaching efficiency. After acid leaching treatment, the LiF content in the aluminum bath decreases from 7.7 % to 0.8 %. The purified electrolyte can be returned to the bath recycling of the aluminum smelter. Large-scale pilot tests have been conducted in Northeastern University with good results.

In the aluminum salt leaching method, aluminum salt, such as $AlCl_3$ or $Al_2(SO_4)_3$, is used to treat the spent electrolyte at high temperature with lithium carbonate (Li_2CO_3), aluminum hydroxyfluoride hydrate ($AlF_2OH \cdot 1.4H_2O$) and HF as the final products. Compared with the acid leaching method, aluminum salt leaching method consumes less acid, and chemicals have less corrosion attack to the equipment, and the process is simple. However, this process should be

operated at high temperature, consequently high energy consumption. The final products cannot be used directly by the aluminum smelters.

4. Conclusions

Even though many new technologies for treatment of solid wastes have been developed in China, very few of them have been put into industrial practice. A good technology, which decreases the toxicity of the solid hazardous wastes generated in aluminum industry and makes solid wastes to reusable raw materials at reasonable cost, is very important for sustainable development of aluminum industry in China.

According to current situation of technological and industrial practice on recycling of solid wastes in China, detoxification of solid hazardous wastes is still the main objective, especially on the disposal of spent refractory, which is send to landfills after meeting environmental standards.

Technologies for transformation of solid wastes to raw materials should be verified by large-scale industrial tests and implementation. From a technical point of view, vacuum distillation technology and flotation-alkaline leaching-acid leaching joint technology are very promising. Their implementation economics should be verified by industrial practice.

In China, companies would like to use mature technologies for treatment of solid wastes at low cost and do not like to develop new technology and conduct industrial test, which slow down the industrialization of emerging technology.

5. Acknowledgements

The work is financially supported by the China Nature Science Foundation Grant under grant No: 51434005, 51529401 and 51474070.

6. Reference

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