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DEVELOPMENT STATUS OF PROCESSING TECHNOLOGY FOR SPENT POTLINING IN CHINA

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Abstract

With the development of Chinese aluminum industry, wastes from smelters are severely restricted by the government. Different processing technologies for spent potlining (short as SPL) have been developed in the past five years. Main SPL processing technologies are Detoxifying with limestone, coal cinder by Pyro-process, Detoxifying with bauxite in Aluminum Sintering Process and Floatation of SPL. Three typical technologies were put into industrial application in Pingguo Smelter, Shandong Smelter and Yichun Smelter, respectively. SPL plant in Pingguo which adopts Pyro-process has a capacity of 15000 metric tons per year. SPL-bauxite Sintering Process used in Shandong can treat 6000 metric tons SPL every year. Floatation of SPL was put into industrial test in Yichun this year and the test scale is 1000 metric tons SPL per year. Different products which were received from three processes can meet national standard, at the same time SPL can be sufficiently detoxified after processing.

Introduction

Chinese primary aluminum industry has gained rapid development in the past eight years. The annual discharge of spent potlining has increased year by year. The average unit discharge of SPL is about thirty kilograms excluding cathode rods. The total SPL discharge had surpassed 2.7 million metric tons by the end of 2008 [1, 4]. There are lots of fluorides in SPL, which exist as Na_3AlF_6 and NaF. Moreover, there is a little of cyanides which exist as NaCN and $Na_4[Fe(CN)_6]$ [1, 2, 4]. SPL leads heavy pollution to the environment due to its high level toxic fluoride and cyanide. Processing of SPL is becoming more and more necessary in order to keep sustainable development of Chinese primary aluminum industry. Many research projects were done to detoxify and recycle SPL. Due to good solubility of sodium fluoride and cyanides, Hydro-process does not receive satisfactory results during processing of SPL, and Pyro-process is becoming dominate method in the world [3]. Different processing technologies for SPL have been developed in China. There are Floatation of SPL and Acid-digestion of SPL which belong to Hydro-process [5, 6]. Chalco-SPL-Process and SPL-bauxite Sintering Process are typical Pyro-process. In the past five years, Detoxifying with limestone, coal cinder by Pyro-process (called Chalco-SPL-Process), Detoxifying with bauxite in Aluminum Sintering Process and Floatation of SPL were developed rapidly. Three typical technologies were put into industrial application in Pingguo Smelter, Shandong Smelter and Yichun Smelter, respectively.

Main Processing Technologies and Their Development Status

Chalco-SPL -Process

Chalco-SPL-Process (process 1#) is a pyro-process and was successfully developed by Chalco in 2005. In process 1#, SPL, limestone and coal cinder are mixed according to stated proportion. Limestone is usually quantified by fluorine content in SPL. Coal cinder is quantified by needed silica according to reactions 4 and 5 (See Table I). Then the mixture is crushed till all granules can go through screen with two millimeter sieve pore. Fine mixture is fed into rotary kiln. Process temperature is 900~1050 ℃. Final products of process 1# are aluminum fluoride and solid residue. Fluorides in solid residue are CaF_2 and $Ca_4Si_2O_7F_2$.Aluminum fluoride can be recycled to reduction cells. Solid residue which contains about 20% calcium fluoride can be sent for cement production. Calcium fluoride in the solid residue can catalyze cement sintering reactions. Thus fluorite is saving. The flow sheet of process 1# is briefly described in Figure 1.

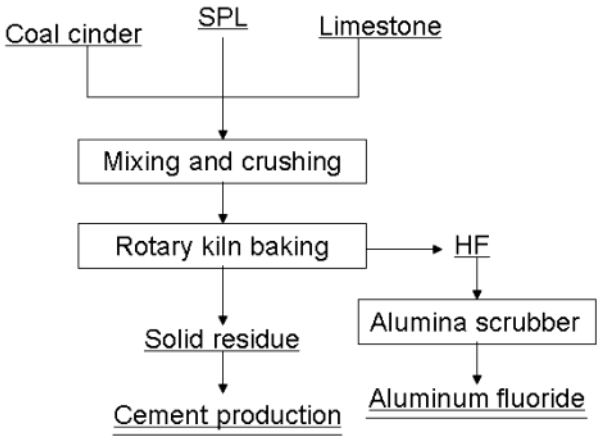

Figure 1. The flow sheet of Chalco-SPL-procss

There is about 30% carbon in SPL, which is used as assistant fuel in Chalco-SPL-process. It is feasible to make full use of heat energy of carbon by intensifying heat transfer in the kiln. Carbon in SPL can combustion fully and provide 70% heat energy for reactions in the kiln if a little of coal is added into SPL. With carbon burning, fluorides dissociate from enwrapping of carbon and become free and active. During processing of SPL, lots of chemical reactions occur. Possible reactions in process 1# are listed in Table I.

Among these reactions, SiO_2 and most of Al_2O_3 come from coal cinder. At high temperature of 900~1050 ℃, decomposition of

cyanides and conversion of fluorides rapidly happen. Therefore SPL can be detoxified and its fluorides can be recycled. A pilot plant with a capacity of 3000 metric tons SPL was set up in Qinyang Smelter, Henan province. From 2006 to 2007, process 1# was optimized. Further research work was performed on how to avoid jam during spent cathode grinding, how to speedup fluorides reaction and how to catalyze carbon combustion. Process 1# was applied to set up a SPL detoxifying plant in 2008. SPL plant locates which belongs to Pingguo Smelter has a capacity of 15000 metric tons SPL per year. The plant is in construction.

Table I Possible Reactions in Process 1#

Number	Reactions
1	$C+O_2=CO_2$
2	$Na_3AlF_6=AlF_3+3NaF$
3	$CaCO_3=CaO+CO_2$
4	$2NaF+3CaO+2SiO_2=CaF_2+Na_2O\cdot SiO_2+2CaO\cdot SiO_2$
5	$2NaF+3CaO+2SiO_2+Al_2O_3=CaF_2+Na_2O\cdot Al_2O_3\cdot 2SiO_2+2CaO\cdot Al_2O_3\cdot SiO_2$
6	$2AlF_3+3H_2O=Al_2O_3+6HF$
7	$2AlF_3+3CaO=3CaF_2+Al_2O_3$
8	$2NaCN+2.5O_2=2CO_2+N_2+Na_2O$
9	$2Na_4[Fe(CN)_6]+15.5O_2=Fe_2O_3+12CO_2+6N_2+4Na_2O$

SPL-bauxite Sintering Process

SPL-bauxite Sintering Process (process 2#) is also a pyro-process. The process can make full use of carbon in SPL. Carbonaceous material is first separated from other materials, then grinded and mixed into coal powder which use as fuel. During processing, cyanides are decomposed and fluorides are changed to calcium fluoride which finally enters into red mud. Flow sheet of process 2# is plotted in Figure 2. Possible chemical reactions related to spent cathode in process 2# can be seen in Table II.

Table II Possible Reactions in Process 2#

Number	Reactions
10	$C+O_2=CO_2$
11	$2NaCN+2.5O_2=2CO_2+N_2+Na_2O$
12	$2Na_4[Fe(CN)_6]+15.5O_2=Fe_2O_3+12CO_2+6N_2+4Na_2O$
13	$Na_3AlF_6=AlF_3+3NaF$
14	$2NaF+CaO=CaF_2+Na_2O$
15	$2AlF_3+3H_2O=Al_2O_3+6HF$
16	$2AlF_3+3CaO=3CaF_2+Al_2O_3$
17	$Na_2O+Al_2O_3=2NaAlO_2$

In general, ten kilograms spent cathode can be processed when per ton bauxite is sintered. Average fluoride concentration in tail gas emitted from process 2# is about 28 mg/Nm^3. There are some tiny sodium fluoride particles in exhaust gas. The process has some merits such as saving some coal, recycling of carbon in SPL and no investment on equipments. But the process throws away valued calcium fluoride. Furthermore, other materials from SPL need safety landfill which brings additional investment. In 2008, SPL-bauxite Sintering Process was applied in Shandong Smelter which locates in Shandong province. Its capacity is 6000 metric tons SPL per year. This year Guizhou Smelter which locates in Guizhou province will put another 3000 metric tons SPL into processing by SPL-bauxite Sintering Process.

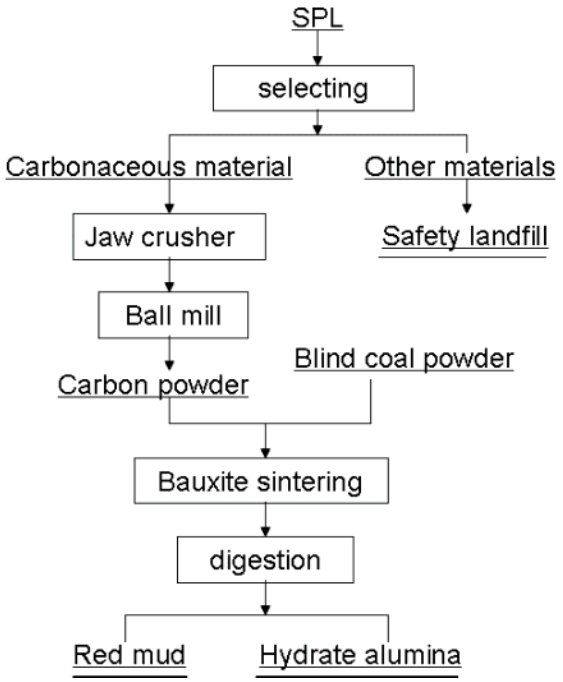

Figure 2. The flow sheet of SPL-bauxite Sintering Process

Floatation of SPL

Floatation of SPL (process 3#) is a hydro-process. The process can recycle carbon powder and fluorides in SPL. During floatation, different medicaments were added to separate carbon powder and fluorides. There are no chemical reactions between floatation medicaments and SPL. But chemical reactions between SPL and water usually occur quickly at room temperature during floatation. The flow sheet of the process 3# is drawn in Figure 3. Possible reactions in process 3# are listed in Table III.

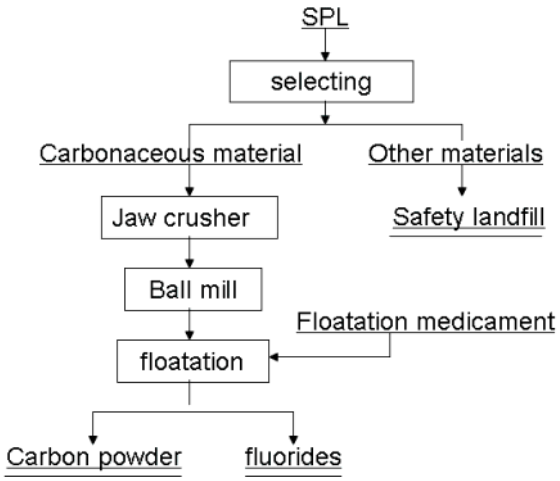

Fig.3 The flow sheet of Floatation of SPL

Table III Possible Reactions in Process 3#

Number	Reactions
18	$NaCN+2H_2O=NH_3+HCOONa$
19	$Na_4[Fe(CN)_6]+6H_2O=6HCN+Fe(OH)_2+4NaOH$
20	$2Na+2H_2O=2NaOH+H_2$
21	$2Al+3H_2O=Al_2O_3+3H_2$
22	$Al_4C_3+6H_2O=2Al_2O_3+3CH_4$
23	$2AlN+3H_2O=Al_2O_3+2NH_3$

Gases from these hydrolyzing reactions are H_2, NH_3, CH_4 and HCN. Floatation of SPL was put into industrial test in Yichun Smelter which locates in Henan province this year. The test scale is 1000 metric tons SPL per year. Although carbon powder and fluorides can be received from process 3#, some shortcomings still restrict industrial application of process 3#. First, waste water from process 3# is harmful because of containing 300 mg/L soluble F^- and 30 mg/L CN^-. But national permitted concentration for F- and CN- are 10 mg/L and 0.05 mg/L, respectively. Waste water must be cleaned and harmless before discharge. Decontaminating of waste water will add cost to process 3#. Secondly, fluorides received from process 3# contain almost 7% carbon so that they cannot be recycled directly to reduction cells. Additional pyro-process is needed to remove carbon from fluorides. Thirdly, carbon powder received from process 3# contains almost 10% fluorides so that it cannot be returned to electrode production and need to remove fluorides. Fourthly, carbon in SPL need strict milling before floatation and milling cost is high. Finally, medicament cost and facility investment are high. These disadvantages make smelters dislike process 3#.

Conclusions

Process 1# which belongs to Chalco has shorter flow than process 2# and process 3#, and it has wider market in China. Process 2# integrates SPL processing and bauxite sintering, although it has no equipment investment, it can only be applied in alumina refinery which has bauxite sintering. So process 2# has small market in China. Process 3# has longer flow and higher cost than process 1# and process 2# so that few smelters would like to use it.

With further development and optimization of these SPL processing technologies, it is feasible to detoxify and recycle SPL in China. Different products which were received from three processes can meet national standard, at the same time SPL can be sufficiently detoxified after processing. The government encourages smelters to process SPL and would like to reduce or release revenue from SPL processing.

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