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Hazardous waste treatment for spent pot liner

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Hazardous waste treatment for spent pot liner

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Abstract. The spent pot liner is the largest solid waste produced by the electrolytic aluminum industry, composed of a series of substances that accumulate in the containers with reduced aluminum during the process of bauxite purification and refining. More and more spent pot liner is accumulated and needs to be dealt with. This paper discusses the composition and harm of solid waste. This paper expounds the comprehensive utilization value and disposition of the waste pot liner.

1. Introduction

The comprehensive utilization of resources and the environmental protection has been a hot topic studied by foreign scholars in China. Strictly controlling the total emission of pollutants is the country's hard demand for electrolytic aluminum industry, as well as an important way for the electrolytic aluminum industry to improve its image for the moment. The waste cell liner is the world's most troubled source of environmental pollution for a long time. According to the statistics, for per ton of primary aluminum produced, about 30 to 50 kg of SPL is generated. Each ton pot liner contains about 150 kg of fluoride and 2 kg of cyanide. Current capacity of aluminum production in an electrolytic aluminum factory is 200,000 tons per year which produces about 6000t waste. Over the past 15 years, the output of aluminum has ballooned, reaching 316.72 million t in 2015, and the total output is 9502 million t. The solid waste produced during the production of electrolytic aluminum can cause serious damage to ecology, production and life without controlling. It is a great challenge for the world's electrolytic aluminum industry to be able to dispose of it and recycle it as recycling resources.

Table 1 Change of aluminum production and waste pot liner emissions (unit: million tons)

Number	Year	Production	Emission
1	2001	341	10.23
2	2002	436	13.08
3	2003	532	15.96
4	2004	630.8	18.92
5	2005	780.6	23.42
6	2006	934.9	28.05
7	2007	1258.8	37.36
8	2008	1310.5	39.32
9	2009	1296.4	38.89
10	2010	1613.1	48.39
11	2011	1778.6	53.36
12	2012	1975.4	59.26
13	2013	2193.6	65.81
14	2014	2394	71.82
15	2015	3167.2	95.02

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2. Pollution and damage

2.1. Solid waste

The biggest solid waste is the electrolytic pot slags and the used lining of the electrolytic aluminum industry (see in figure 1 and figure 2). The main composition and content of the slag are shown in figure 3. Main including: spent cathode carbon block, cathode paste, insulation brick, firebrick etc.

Fig.1 Electrolytic cell spent lining

Fig. 2 Overhaul slags of the electrolytic cell

The spent cathode contains a lot of fluoride and cyanide. Fluoride is brought in by aluminum fluoride and cryolite. The waste of cathode carbon block can't store up, one of the main reasons for containing a large amount of fluorine. The formation of cyanide is mainly caused by the infiltration of air through openings in the pot shell and the nitrogen in the air subsequent reacts with the cathode carbon block.

Two compounds are commonly produced, one is NaCN, the other is Na4Fe (CN), and the concentration of the cyanide is more than 1%.

2.2. Pollution of Solid waste

If not handled electrolytic cell solid waste, fluoride flows with rain water and contaminates surface water and underground water system, will eventually cause great harm contribute to the animals, plants and people, as shown in figure 4.

(1) Hazardous gas pollution. On the one hand, under atmospheric erosion, the solid waste surface is polluted by the toxic dust from weathering. On the other hand, the waste grooves and water are prone to react in the case of normal temperature and pressure. And they react violently and release a lot of gas. The pungent odour is often smelled when the waste tank met with rain or water. The main reaction of the SPL and water:

$$\mathrm{CN}^{-} + 2H_2O = \mathrm{N}H_3 \uparrow + HCOO^{-} \tag{1}$$

$$[\mathrm{Fe(CN)_6}]^{4-} + 6H_2O = 6\mathrm{HCN} \uparrow + \mathrm{Fe(OH)_2} \downarrow + 4OH^{-} \tag{2}$$

$$2\mathrm{AlN} + 3H_2O = \mathrm{Al}_2O_3 + 2\mathrm{N}H_3 \uparrow \tag{3}$$

$$\mathrm{Al_4C_3 + 3H_2O = 2Al_2O_3 + 3CH_4} \uparrow \tag{4}$$

(2) Water pollution. Spent cell lining contains large amounts of fluoride and cyanide and other toxic substances. If not treated with effectively and direct emissions will seriously affect the underground water quality and have the great effects on the water surrounding the electrolytic aluminum industry.

(3) Soil pollution. Waste pot lining belongs to high-risk waste. Improper handling with waste cell lining can cause secondary pollution, such as pot liner and refractory materials piled up in open pit. It will be causes infiltration of soluble fluoride and cyanide because of the snow and rain erosion and pollutes underground soil

(4) Biological destruction. It is harmful to the growth of animals and plants, and its characteristics are great toxicity and fast effect. For plants, plant tissue becomes black and necrotic, destroying agricultural ecological balance and reducing crop production. Animals poisoning, respiratory failure, suffocation or death, the main reason is that the cyanide can enter the body through the mouth, respiratory, or skin, immediately hydrolysis for hydrogen cyanide acid is absorbed under the acid dissociation. After the cyanogen enters the circulation of the blood, it is combined with the cytochrome Fe3 + in the blood, and produces the cyanoferricytochrome oxidase. The loss of the ability to transmit electrons break down the respiratory chain and causes the cells suffocate.

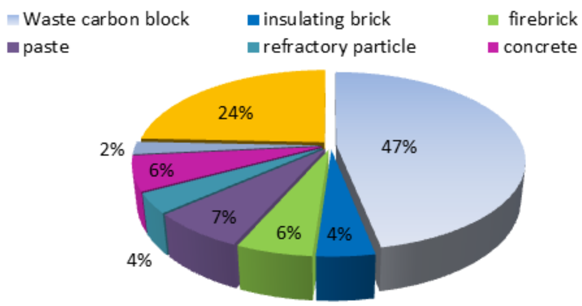

Fig. 3 Composition and content of Overhaul slag

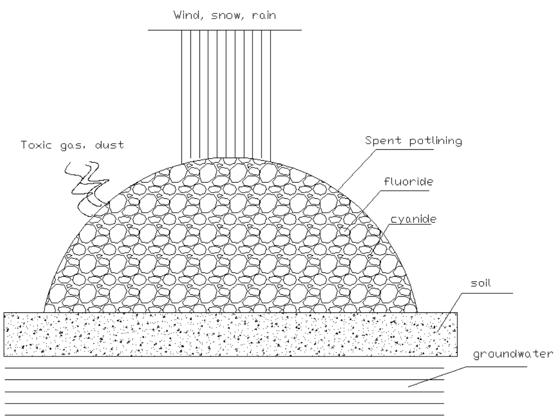

Fig. 4 Hazards of solid waste in electrolytic cell

3. Comprehensive utilization values

3.1. Production of high graphite cathode carbon blocks with waste pre-baked anode carbon.
The research shows that the electrolytic aluminum cathode carbon is gradually improved by the electrolytic temperature and electrolyte catalysis. After 3 to 8 years, carbon has graphitized, graphitization degree has been raised from about 80% to 95% at elevated temperature of 800-900℃ for several years, it has reached a very graphite-high synthetic graphite. High quality graphite cathode carbon blocks have been tried in industrialization in 300KA aluminum electrolytic pilot plant, the cathode voltage drop by 30 ~ 50 mv compared with contrast slot. The results are expected to saving power about 80 to 100 kwh/t. al. Improved cell life between 100 and 150 days. Reducing the emissions of the waste cell lining is good for ecological environment protection.

3.2. As a fuel for cement manufacturing
Waste carbon block after crushing in cement clinker kiln can replace part of the fuel and save energy. Fluoride can be used as mineralizer to improve kiln firing conditions, fluorine generated solid-state CaF2 into the cement, and it will not pollute the environment and achieve the purpose of comprehensive utilization. There are cement factories all over the place, so there are more extensive use conditions.

3.3. As a substitute for molten iron blast furnace
As a substitute, used limestone and fluorite as flux in the cupola. The effect is to reduce the melting point and viscosity of slag. Fluorite CaF2 is an expensive mineral material. A large amount of fluoride is found in the slag of the electrolyzer, so it can be used as a flux.

3.4. The value of elements and compounds
Rich carbon, fluoride and other substances in the SPL (see table 1, figure 5). And sodium fluoride, cryolite is important industrial fluorine products, mainly used for electrolytic aluminum, wood preservation, electric welding, pesticide, fungicide, and preparation of fluorine and other products, so the use value is very high. After fire disposal the waste cell lining, calcium fluoride melting slag can be used as road filling materials and production of cement or refractory. Recycling of fluoride salt can return cell to use.

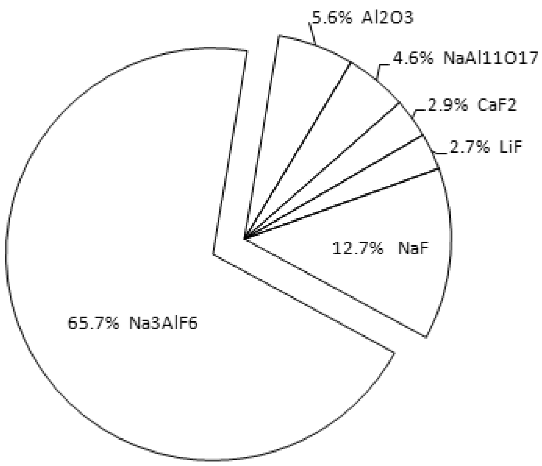

Fig. 5 Composition of major slags in electrocell

Table 2 Main chemical elements of spent cathode carbon block (unit percent)

Chemical Composition	C	Na	F	Al	Ca	Fe	SiO_2
Content (%)	58.56	11.86	9.86	2.42	1.36	0.74	4.33

4. Processing method

There are two main requirements for the disposal of the used lining. One is harmless and the other is recycling. Harmless mainly treatment of fluoride and cyanide; Recycling is a way of separating the useful components from different processes.

At present, there are many ways to deal with waste cathode lining. it can be divided into several categories: (1) According to the physical properties of the substances, such as solubility, surface properties and density, the carbon and fluoride are separated;(2) Using heat treatment to deal with corrosion-resistant substances, such as carbon, which can be burned at high temperature; (3) chemical extraction and other methods are used to treat fluoride and cyanide.

4.1. The treatment technology of the wet process of electrolytic cell

The technique is mainly to mix the electrolyze overhaul slag with the bleach powder. The cyanide is decomposed by hypochlorite. Fluoride reacts with water soluble calcium and magnesium ions and aluminum ions in the slurry to generate non-toxic CaF2, MgF2, AlF3 precipitation. Centrifugal separation, solid-liquid separation or filter sedimentation pond separation is adopted. The separated water can be used for the pretreatment process. The deposited solids can be used for additives or refractory material production or building materials.

4.2. Foam flotation process

By using the difference of hydrophobic water between carbon and electrolyte, the two kinds of valence components are better separated. Each substance the purpose intended. The method is simple, economical and efficient and has a good development prospect. Flotation carbon powder can be used as cathode addition of aluminum reduction cell. It is advisable to add 20% to 20%, Floatation electrolyte through 600 ℃, firing purity can reach 99%, the purity of floatation electrolyte after 600 ℃ calcination electrolyte can amount to 99%, it can be used as a raw material or new electrolytic cell mixed with a small amount of cryolite used in aluminum electrolytic cell, The flotation wastewater was emission on standard after treatment with bleaching powder. The process of wet process can precipitate the highly toxic HCN and HF gas. They Cause serious equipment corrosion and pollute the environment and harm to human health, so it's hard to industrialize

4.3. Fire treatment technology

The decomposition condition of the burning of hazardous substances is controlled by adding additives such as fly ash, limestone and other additives after crushing the spent pot lining. Including cyanide about 99.5% at 300 ℃ can be decomposed to disappear, disappear when heated to 400 ℃ about 99.8% decomposition, and can achieve 100% to more than 700 ℃ when the decomposition.

Fire treatment technology has the characteristics of simple process, less investment, and thorough treatment of harmful substances. Therefore, the technology of fire treatment is the leading direction of waste pot lining.

$$4\mathrm{NaCN} + 9O_2 = Na_2O + 2NO_2 + 2CO_2 \tag{5}$$

$$2\mathrm{NaCN} + 4\mathrm{O}_2 = \mathrm{Na_2O} + \mathrm{N_2O_3} + 2\mathrm{CO}_2 \tag{6}$$

$$2\mathrm{NaF} + \mathrm{Si}O_2 + CaO = CaF_2 + Na_2O \cdot \mathrm{Si}O_2 \tag{7}$$

$$2\mathrm{NaF} + 2\mathrm{Si}O_2 + 3CaO = CaF_2 + 2CaO \cdot SiO_2 + Na_2O \cdot SiO_2 \tag{8}$$

4.4. Landfill method

The landfill method is the main method of disposal of the slag in our country. In view of the waste cell lining belongs to high-risk waste, electrolytic aluminum industries should strictly follow the storage and management of hazardous waste storage pollution control standards. The landfill is composed of natural base layer, impermeable layer, double artificial lining and composite lining (figure 6). Landfill must be set impervious layer in order to effectively prevent the leakage of hazardous substances, and set the leachate collection and drainage system, rain water drainage system and exhaust system, effectively prevent the landfill content of soil, groundwater and atmosphere.

The main disadvantages of this disposal method is taking up a lot of land and causing a lot of waste of land resources. Secondly, there are hidden dangers of pollution, and the toxic and corrosive effects of harmful substances in spent cell lining.

If the treatment is not good, it will pollute the underground water system and harm the future generations. Third, it is very difficult to prevent the corrosion resistance of the infiltration layer, the construction is difficult and the cost is high. This method will not adapt to the increasingly urgent environmental requirements and sustainable development, It will be eliminated eventually.

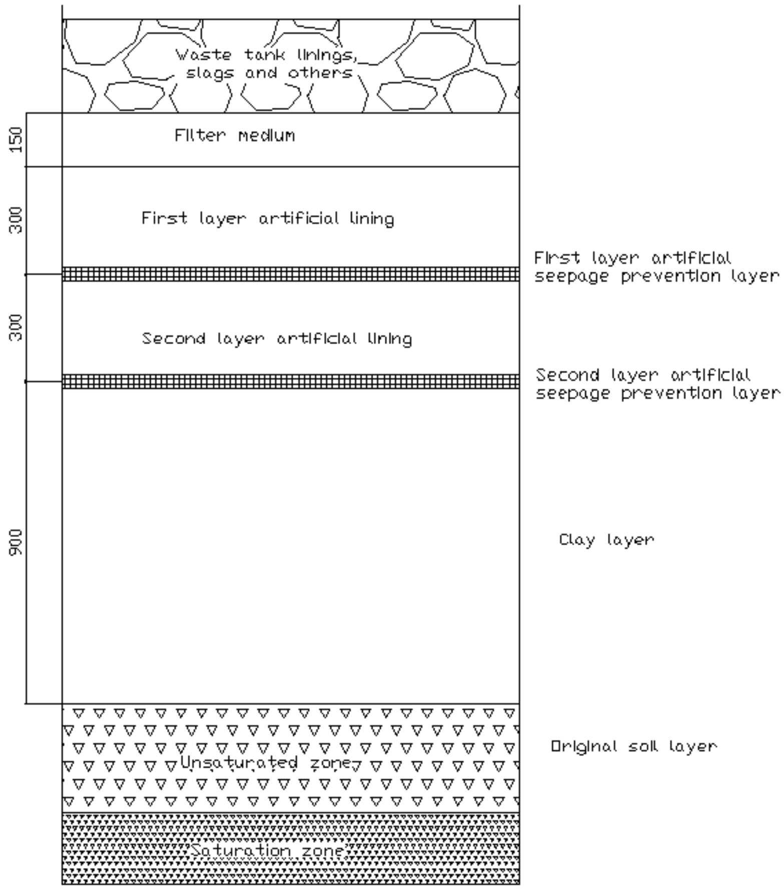

Fig 6 Landfill requirements of electrolyzer solid waste

5. Conclusion

How to reduce the amount and harm of electrolytic cell solid waste, we need to be supported by scientific and technological innovation, Constantly to improve design, selection and the key to develop management plan, as far as possible the most greatly make waste recycling, not only contribute to environmental protection, but also to decrease the cost of enterprise management. In addition, advanced technology and equipment should be adopted to improve management. To enhance the optimization of electrolytic aluminum production process by careful operation and investment in environmental protection equipment. It is a necessary way to develop the environment-friendly electrolytic aluminum industry by extending the life of the electrolyzer as far as possible, reducing the number of slots and controlling the emission of pollutants.

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