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Study of recycling and treatment methods spent pot lining (SPL)

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Abstract

In this study, a summary of the processes performed on the SPL for recycling, reduction in toxicity and treatment were examined on an industrial and laboratory scale. In writing this research, an attempt has been made to address the useful processes that have taken place in this field. Spent pot lining or SPL is a type of solid waste that is produced in the aluminum production process. After 3 to 8 years, the cathode blocks become problematic and can no longer be used, and need to be replaced due to adverse effects on cell function. SPL is known to be a hazardous waste to nature due to its fluoride and cyanide content. Research has shown that SPL ingredients have destructive and very dangerous effects on human DNA, which is why they are so important to maintain and recycle.

Key words: Spent Pot Lining, SPL, Aluminium, Recycle, Toxicity

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1. Introduction

So far, a lot of research has been done on SPL. Spent pot lining (SPL) are hazardous waste produced in the rooms of aluminum smelting cells. According to research by Andrade-Vieira et al., SPL is a hazardous waste that can cause genetic damage to human DNA due to fragmentation and mutations [1]. In this study, we try to examine the origin, composition, and methods of excretion and recycling of SPL.

In the process of aluminum production, we add alumina to the electrolyte of Hall-Héroult cells, which produce aluminum metal by the reaction of alumina and electrolyte. This process is done by inducing an electric current. In this way, the electric current enters the cell through carbon anodes and after passing through the electrolyte, it enters the graphite cathodes and leaves the cell. Cell electrolyte composed of cryolite (Na_3AlF_6) and alumina (Al_2O_3) which maintains a temperature of about 960 ° C [2]. Due to the impregnation of graphite cathode blocks with fluoride-containing salts and other chemicals in the aluminum production process, the cell has a problem after 3 to 8 years and can no longer continue to work, in whichcase carbon dioxide (pot lining) It is removed from

The cell and the shell is repaired. The resulting waste material is called spent pot lining, or SPL for short, which consists of two parts, the first part which is rich in carbon (the first cut) and the second part which is mainly made of ramming paste, refractory bricks and insulated bricks [3, 4]. We are interested in the first cut because it contains minerals such as Na_3AlF_6, NaF, Al_2O_3, $NaAl_{11}O_{17}$, CaF_2 and Graphite [5]. The available elements and their percentage are described in Table 1. There are various opinions about the production of spl in the cell for the production of each ton of aluminum. Usually in Soderberg's produce, 35 kg(SPL)/ton(aluminum) and prebakes 20-28 kg(SPL)/ton(aluminum) and figures may vary depending on lining life achieved. In prebake cathodes, lining will generally last about 1,700 to 2,200 days with graphite blacks, 2,700 to 3,000 days with amorphous carbon blocks, and about 2,400 days with semi-graphite blocks. Due to the change in amperage, the amount of aluminum produced during the working life of the cell is not constant, so to determine the amount of SPL produced per ton of aluminum, it is necessary to observe this case and accurate calculations [3, 6, 7].

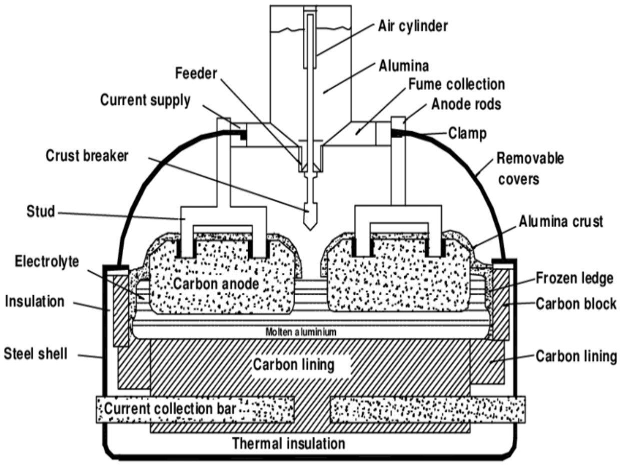

Fig. 1. Schematic image of Hall-Heroult cell [8]

As we know, the period of cell function is a very important factor that causes different SPL compounds. Intercalations of Sodium and Sodium Fluoride inside the lining materials increase with longer cell operation. The SPL for the three different technologies, including Type A, Type B, and modern prebakes, is shown in Table 1. As can be seen in Table 1, the amount of fluoride ions and the concentration of cyanide also depends on the technology and other factors.

Table 1: SPL composition for different technologies [9]

Elements	**A type**	**B type**	**Soderberg**	**Major phases**
Fluorides (wt. %)	10.9	15.5	18	Na_3AlF_6, NaF, CaF_2
Cyanides (ppm)	680	4480	1040	NaCN, $NaFe(CN)_6$, Na_3FeCN_6
Ratio (HCN/Total)	2.7	1.9	3.4	
Aluminum total (wt. %)	13.6	11	12.5	Al_2O_3, $NaAl_{11}O_{17}$
Carbon (wt. %)	50.2	45.5	38.4	Graphite
Sodium (wt. %)	12.5	16.3	14.3	Na_3AlF_6, NaF
Al metal (wt. %)	1	1	1.9	Metal
Calcium (wt. %)	1.3	2.4	2.4	CaF_2
Iron (wt. %)	2.9	3.1	4.3	Fe_2O_3
Lithium (wt. %)	0.03	0.03	0.6	Li_3AlF_6, LiF
Titanium (wt. %)	0.23	0.24	0.15	TiB_2
Magnesium (wt. %)	0.23	0.09	0.2	MgF_2

Because SPLs have a high operating temperature, some water-reactive chemicals are formed during cell life. As a result, a variety except for fluoride, sodium, and aluminum compounds, SPL also contains cyanides, metals (Al, Li, and Na), reactive metal oxides (Na_2O), carbides, and nitrides [9]. The various compounds mentioned reacting with moisture to form NaOH, H_2, C_2H_4, and NH_3. Before, the SPL water reactivity was used to break loose the lining by soaking the complete cell in water. In any case, because of health safety and environmental (HSE) [10] concerns, They don't do that anymore, and today the lining is removed dry. The active nature of the material makes it possible:

1. Toxic: Fluoride and cyanide compounds those are leachable in water
2. Corrosive: High pH due to alkali metals and oxides
3. Reactive with water: Producing inflammatory, toxic and explosive gases

Therefore, due to the toxic properties, corrosion and reactivity of this material, care must be taken in its use, storage and transportation, and serious measures must be taken.

Methods

Lately storage of SPL

The method of SPL storage depends on its classification according to the law of each country, such as special, industrial or hazardous waste. Based on current production levels, Can be estimated that a significant amount of SPL more than>50% is still stored in buildings lined and unlined sites, waiting for treatment. If we consider China as well, this amount will be more than 75% [9]. A method that can be considered as an inactive solution in Norway and Iceland where SPL has been stored on the seashore allowing sea leaching of soluble components. The leachable fluorides present in SPL will react with the calcium ions in seawater to form stable calcium fluoride. An extensive investigation by the University of Iceland did not indicate that the dumping pits had detrimental effects on onshore communities [17].

Industrial methods of Spent Pot Lining

Industrial methods of Spent Pot Lining the uses in various industries has been investigated and some the possible uses are highlighted in Table 2.

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Table 2: Use of SPL in industries

Industry	Approach and reason	Disadvantage or problems associated	Location
Cement [7, 11-13]	To use first cut SPL in the kiln as it has reasonable calorific value and fluoride reduce the kiln temperature Second cut used in cement kiln	1- Necessity for 2- Transportation in a closed container 3- Maximum allowable limit for sodium (< 0.6%) and fluoride limits the additions up to a few percent of the feed stock	Brazil
Steel [14-16]	Additive to steelmaking because fluoride improves slag formation and small quantities of SPL can substitute for CaF_2	1- Necessity for Transportation in a closed container. 2- Limitation of use due to hazardous waste	Italy

Recovery and Treatment Processes

Yet many processes have been developed, out of which pyrometallurgical or hydrometallurgical processes found to be suitable.

Industrial-scale improvements

Different types of furnaces have been tried, including rotary kilns, coffee roasters, and specialized and arc furnaces at various temperatures. Examples of the industrial-scale treatment process are shown in Table 3.

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Table3: The industrial-scale treatment process for SPL

Treatment approach	Process condition and purpose	Advantages	Disadvantages
PYROMETALLURGY APPROACH			
ALCOA (Reynold) Gum Spring process [18]	Destruction of cyanides in a rotary kiln and creation of industrial waste for road aggregates Use of Limestone to fix fluorides	Generation of inert materials	High temperature treatment approach High cost for the treatment
RT (Comalco) COMTOR [9, 19, 20]	Destruction of cyanides in a pretreatment reactor. Residue is leached with lime to produce a Bayer-type liquor and kiln-grade Spar for the cement industry	Generation of product used in other industry	High temperature treatment process leading to high energy demand
AUSMELT process [7, 9, 20, 21]	Formation of AlF_3 and reusable industrial waste	Moderate quality of Product	High energy demand
VORTEC Process [9, 10, 20]	Generation of reusable Industrial inert waste by combustion and pyrohydrolysis process	Moderate quality of product	High energy demand
NOVA Pb [9]	Treatment in rotary kiln at 1000°C	Formation of useful product i.e. Calcifrit (High Fluoride and aluminosilicates) and Calcicoke (High Carbon)\ Potentially recyclable products	High treatment cost
Regain Process [9]	Partial detoxification of SPL	Low temperature process for the destruction of simple cyanides to deactivate SPL	Still hazardous material
ELKEM Process [7, 22]	Use of SPL as a feedstock for pig iron making	As feedstock material	Transportation problems and less requirement of feed
SPLIT Process [9, 20, 21]	Treatment of SPL with $CaSO_4$ at 1000°C	Production of inert materials	High treatment cost
Plasma verification [9, 21]	Inertization of SPL at high temperature	Generation of inert materials	High temperature treatment
HYDROMETALLURY APPROACH			
BEFESA [9]	Co-processing of SPL with salt slags	Formation of suitable components to be used in cement or mineral wool industry Low temperature treatment process	Not Available

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RIO TINTO ALCAN [7, 9, 23, 24]	Low caustic leaching and Liming	Formation of Bayer liquor , CaF_2 and industrial waste can be used in other industry Low temperature treatment approach	High installation cost

Table 4: Lab-scale pyrometallurgical approach for SPL

Sl.	PYROMETALLURGY APPROACH		
No	Year	Authors	Approach and Findings
1	1997	V. A. Utkov et al [25]	Water soluble NaCN was neutralized by treating carbon rich part with an $FeSO_4^-$
2	2000	Wang Y	Crushed first cut SPL can be used as collar paste for protecting anode stems.
3	2000	Oliveira et al [7, 8]	Heating of second cut SPL up to more than 750°C to remove molten and volatile impurities
4	2000	Balasubramanian et al [7, 26]	Vitrification of SPL by adding small additions of glass former along with traces of nucleation agents to aid crystallization and then melting at around 1300°C.
5	2001	Courbariauxet al [7, 20]	Treatment of crushed SPL in a circulating fluid bed
6	2004	Karpel S [7, 21] Li and Chen [5, 7, 9]	Heating of crushed SPL mix to about 1000°C and adding lime to oxidize cyanides and bind the fluoride
7	2007	Lazarinos [7]	Destruction of cyanide compounds in a gasification combustions.
8	2007	Chen and Li [5, 7, 9]	(i)Presence of graphite and sodium in SPL make it sticky, slippery and difficult to crush (ii)Chemical stability of the fluorides in the SPL
9	2009	Blinov et al [7, 8]	Pyrohydrolysis process to recover fluorine as HF and use of carbon rich part in pig Iron manufacture

Lab-scale improvements

A lot of research has examined to mitigate the harmful effect of SPL by employing different approaches and tables 4 and 5 summarize this research.

Table 5: Lab-scale hydrometallurgical approach for SPL

Sl. No.	HYDROMETALLURY APPROACH		
	Year	**Authors**	**Findings**
1	1999	Baranovskii [7]	Mixing of crushed first cut SPL with that of limestone and then adding this mixture to an aqueous slurry for recovery of Soda and Potash
2	2001	Lu et al [7]	Separation of aluminum electrolysis carbon froth and spent pot lining by froth flotation technique
3	2001	Zhao [27]	- Treatment of SPL with water and H_2SO_4 to recover HF - The liquids are filtered for the manufacture of graphite powder, aluminum hydrate and alumina. - Fluoride and sulfates are manufactured from filtrates
4	2001, 2002	Silveira et al [14, 28]	- The leaching behavior of SPL was studied - pH of SPL was around 10-11.8 - Total fluoride content was 5.13-11.41% - Total dissolved fluoride at pH 12 and at pH 5 was 6.45- 9.39% and 0.26-3.46% respectively
5	2002	Mirsaidov et al [7]	Use of pine oil and kerosene as a flotation agent to separate cryolite alumina concentrate followed by burning of remaining carbon at 800°C in rotary Furnace.
6	2007	Lisbona and Steel [29]	Determination of Leachability of NaF, CaF_2 and cryolite from SPL Precipitated fluorides in a form that can be recycled back into the pot have been studied by manipulating solution equilibria.
7	2008	Lisbona and Steel [21]	- Fluoride extraction of 76-86 mol. % by using 0.34 Al^{3+} solution at 25°C for 24 h - Removal of NaF and Na_2CO_3 from SPL by water washing of SPL - In pH 4.5-5.5 selective precipitation of fluoride as an aluminum hydroxyfluoride hydrate product achieved by neutralization - Higher pH leads to co-precipitation of hydrolyzed sodium fluoroaluminates
8	2012	Lisbona et al [30, 31]	- Leaching with Al^{3+} salts to precipitate aluminum hydroxyl fluoride hydrate - Development of low-carbon environmentally sustainable approach

9	2012	Zhong-ning et al [5]	- Two step alkaline-acidic leaching was conducted to achieve 65% leaching rate after NaOH treatment having 72.7% purity of carbon Leaching rate was increased up to 96.2% and purity of carbon up to 96.4%. - Cryolite precipitation rate was 95.6% and purity of Na_3AlF_6 obtained is 96.4%.
10	2013	Lisbona et al [32]	- Leaching behavior of SPL with aluminum nitrate and nitric acid - Following an initial water wash, a single leaching step using 0.5M HNO_3 and 0.36M $Al(NO_3)_3$ at 60°C extracted a total of 96.3% of the remaining fluoride, extraction of Mg and Ca in form of MgF_2 and CaF_2.

Conclusions

Due to the entry of legislators into the issue of storage and disposal of SPL in the aluminium industry, this waste has been identified as hazardous waste for human health. However, so far no extensive advanced technology has been introduced for the recycling of SPL, one of the reasons for which is their unknown chemical behaviour. In recent years, studies on hydrometallurgical methods for the treatment of SPL have increased because it is claimed that these methods require less energy and recover compounds better. So far, no chemical reagents have been found to chemically leach for the recovery of fluoride and graphite carbon from SPL. Overall, there is promising research in this area, and we can hope to see more progress in the future.

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Compliance with ethical standards

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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