AL17 - Minimizing SPL Generation via Redesigning Pot and Life Enhancement

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Abstract

Primary aluminium production process poses a threat to the environment due to generation of hazardous waste like the spent pot lining (SPL). This has led the researchers to focus on 4R (Reduce, Recycle, Recover, Reuse) approaches to minimize the impact of SPL on the environment. Worldwide aluminium smelters have been looking into ways to reduce the SPL generation per tonne of Al produced, such as enhancing pot operational life, as well as by reusing and recovering value from SPL by its utilization in both cement and ferrous industries as well as coal-fired power plants. Hindalco's Hirakud smelter has also been utilizing the 4R approaches with a goal to minimize the SPL impact on the environment. This paper highlights the redesign approach adopted by Hirakud smelter, which has led to reduce the SPL generation significantly. The paper describes the modification in the cell lining design and materials to enhance pot performance and pot life, thereby reduce the SPL generation from 20.41 kg/t Al to about 15.55 kg/t Al. To enhance the energy efficiency of pot, copper-insert collector bars have also been utilized, which are reported to enhance the pot life, thereby further potential of reducing the SPL generation to the level of 14.14 kg/t Al. Apart from the redesign, other approaches such as recycle, recover and reuse have also been looked upon for effective SPL management.

Keywords: 4R approach, pot life, cell lining, spent pot lining (SPL), aluminium smelter.

1. Introduction

Primary aluminium is produced using an electrolytic process, also known as Hall-Héroult process, from the alumina dissolved in to the molten cryolitic bath. The electrolytic process occurs in a steel pot, which is lined with refractories, to offers mechanical and chemical stability. The lining refractory is typically made of two layers, an insulating refractory, which house a carbon cathode along with collector bar to allow the current flow. The cell usually operates for about 4 to 8 years before it fails. The life of the cell usually varies from plant to plant based on the cell technology & operational amperage. There are various factors, which affect cell operational life, e.g., cell design, quality of lining materials, preheating, start-up procedures and thermal disturbance during cell operational life. Precise start-up procedures and efficient operation play key role in attaining a satisfactory life of a cell. The thermal, mechanical and chemical properties of cathode and lining materials may also lead to failure, if the cell is not designed correctly to ensure isotherms in proper locations. Figure 1 shows a typical cross-section of a Hall-Héroult cell, highlighting cell-lining materials such as carbon cathode, refectory and insulation materials. The cell lining design should ensure that the electrolyte freezing isotherm in the lining (~780 °C) should be just below the cathode blocks into the high dense refractory brick, made of silica and alumina. Due to capillary action, bath impregnation takes place after the sodium front has moved through the carbon and only through the porous network formed by the volatilization & shrinkage of the binder during baking [1]. A freezing isotherm inside the carbon blocks may result in frost heave damage and a freezing isotherm too far down into the insulation refractory layer results in damage of the insulation layer, which is usually less dense and less salt resistant then the upper refractory layer. The thermal conductance of the sidewalls should result in a proper ledge shape and thickness.

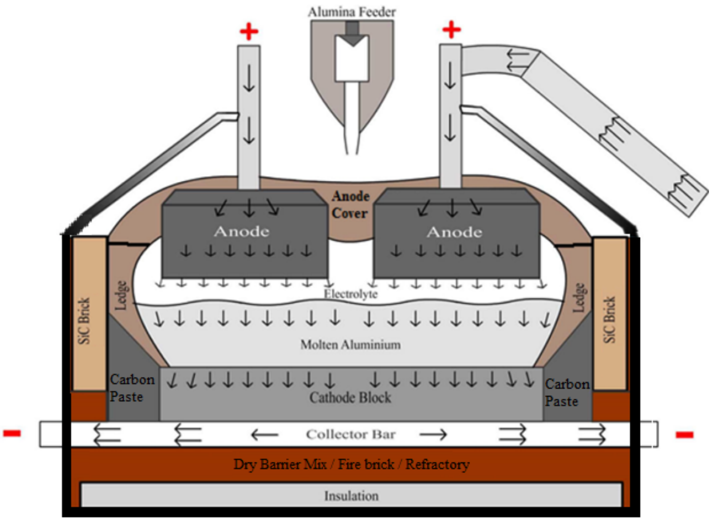

Figure 1. Cross-sectional view of Hall-Héroult cell.

2.1. Role of Cathode in Pot Failure

The pot life depends on various factors, like cell design, lining material, preheating & startup as well as the operational variations encountered during the entire pot life. Regarding materials, along with refractory and insulation, the cathode plays an important role in deciding pot life. Three types of cathode blocks are presently being used in the aluminium industry, for example, anthracitic / semi-graphitic (with 30 %, 50 % or 70 % graphitic content), 100 % graphitic & fully graphitized. Impregnated, fully graphitized cathode block is the recent development to reduce the open porosity in the cathode block, which has positive impact on enhancing pot life, despite resulting in additional costs. Each type of cathode block has its own pros & cons with respect to their properties, which are mentioned in the following Table 1.

Table 1. Relevant properties of cathode block for pot life [2].

Cathode Block Properties	**Semi Graphitic (30–50–70 %)**	**100 % Graphitic**	**Fully Graphitized**
Apparent density (g/cm^3)	1.54–1.63	1.59–1.64	1.62–1.63
Open porosity (%)	15–20	18–22	21–23
Total porosity (%)	20–23	24–25	26–28
Electrical resistivity at 1000 °C (μΩm)	18–26	16–20	10–12
Thermal conductivity at 1000 °C (W/mK)	14–13	22–18	50–40
Cold crushing strength (MPa)	27–27	25–26	20–26
Thermal expansion coefficient at 20 – 520 °C (x10^{-6}/K)	3–3.5	2.9–3.4	2.9–3
Sodium swelling (%)	0.35	0.25	0.1
Wear resistance	High	Medium	Low

There are certain phenomena related to cathode and its properties that may lead to pot failures, for instance, wear of cathode surface, Na diffusion and intercalation, pothole formation etc. Wear rate of cathode is also dependent of current density [3]. Most of the current tries to concentrate towards the end of cathode block due to the least resistant path of electrical current, in such a way that the cathode top surface acquires a W-shape pattern after completion of its normal life. To avoid this, the collector bar assembly-to-cathode block electrical resistances ratio may be modified by means of altering both materials and design. Copper-insert collector bar (CuCB) tends to provide (a nearly) uniform current distribution, which aids in enhancing the pot life [4].

On the other hand, the less graphitic forms of carbon cathode, such as semi-graphitic, have higher level of fermi energy due to disordered structure, resulting in higher Na intercalation as compared to fully graphitized cathodes, which have ordered structures [5]. The Na diffusion may happen either by pure volumetric diffusion inside the carbon grain boundary or by gaseous diffusion inside the pore network of the material. Because of Na penetration, several detrimental effects may happen like cathode swelling, also known as sodium swelling, due to the formation of intercalation compound and subsequently its adverse impact on pot life. The sodium penetration has positive correlation with high bath ratio ($3NaF/AlF_3$) as well as with higher current concentration on the cathode surface. The sodium swelling effects are mostly observed in semi-graphitic cathode type, whereas its impact on fully graphitized cathode is negligible.

The chances of pothole formation are more in amorphous or semi-graphitic cathodes as compared to fully graphitized cathodes due to their heterogeneous structure. In addition, it has also been reported, that most of the potholes were found at the edge of the freeze or ledge toe under the anode shadow [6]. The ledge melts and reforms in a cyclic manner with the fluctuations of cell superheat during several operational events such as metal tapping, anode changing and anode effects. This freezing and thawing process causes the cathode surface subjected to fluctuating stresses, which may in turn cause cracks to form as a potential site for pothole formation. After initiation of a crack, it grows because of the swirling in molten metal, which has been formed because of the combined effects of movement of the metal pad & horizontal component of current flowing down the hole across the cracks, leading to the formation of a pothole.

The Hirakud potline has end-to-end cells with upstream risers, which offer uncompensated magnetic field, leading to higher metal velocities and MHD instability [7]. These pots utilize semi-graphitic cathodes (30% graphite) and old lining design with a tendency to form a ledge toe extension under anode shadow, which increases the chance for pothole formation. There were also operational disturbances like anode spikes, bottom sludge and muck, which may aggravate the pothole formation. These are the some of the factors which have adversely affected the life of Hirakud pots, resulting in higher SPL generation. In this study, these aspects have also been looked upon carefully, while redesigning the cell lining to enhance the performance and pot life thereby reducing the SPL generation. These modifications have been discussed in subsequent sections.

2.2. SPL Management

After the completion of cell operational life, the used lining of the pot is classified as spent pot lining. The SPL is composed of a first-cut (the carbon lining) and a second-cut (the remaining refractory lining). Hundreds of thousands of tons of SPL are stored around the world awaiting a suitable means for their disposal. Disposal of SPL is the foremost environmental problem of the aluminium industry [8]. During the production of one ton of aluminium, a smelter produces about 25 kg of SPL waste with high content of carbon fluorine compounds, alumina, various cyanides, aluminium nitride, aluminium carbide, etc. [9]. In general, fluoride is present in both carbon and refractory layers at around 1–2 wt. % whereas cyanide (CN) content in SPL is low and varies across cuts, though on average CN is around 60 ppm by weight [10]. RTA has developed a process known as Low-Caustic Leaching and Liming (LCL&L) for the treatment of spent pot lining. The hydrometallurgical treatment detoxifies SPL and produces inert by-products, which are subsequently used as raw materials in cement or other industries [11].

The hierarchy of SPL management focus first on reducing the generation itself, by means of redesigning and enhancing the pot life. Subsequently, the preference should be given in descending order to recycle, recover and reuse. The last option is responsible disposal, in which care must be taken on adoption of appropriate storage, handling, treatment, transportation and disposal processes. Hence, the 4R approach (Reduce, Recycle, Recover and Reuse) is adopted for SPL management to minimize the impact on environment, which are described as follows:

a) Reduce or minimizing SPL generation through redesign of pot and optimization of the process;
b) Recycle by using the part of the old pot lining material in a new pot [12] or restarting a stopped or shunted pot by means of patchwork, to utilize the same pot lining material;
c) Recover by conversion of carbonaceous part of SPL into useable heat, electricity or alternate fuel, e.g., use of first-cut material in coal-fired power plant;
d) Reuse by utilizing SPL waste into ferrous, non-ferrous and cement industry. Example of using SPL in cement and ferrous industry has been discussed in the following section.

The first cut of SPL, *i.e.*, the carbon or graphite part, can be used partially as a reductant or alternative fuel for coke in power plant and cement industry. In cement industry there is a relationship between the process temperature in the kiln and the amount of fuel required. Adding SPL increases the amount of fluoride in the raw material, decreasing the temperature requirement, which in turn lowers the coal requirement. The lowered reaction temperature can reduce the amount of fuel coal required also lowering the emission of CO_2 and NOx [10].

The second cut of SPL has found its use in ferrous, non-ferrous and cement industries. For instance, CaF_2 in SPL can be accepted by metallurgical slag as flux, since it can improve the fluidity of most of the metallurgical slags [13]. The silicon, aluminium, iron, calcium, and magnesium oxides present in SPL, can replace the traditional cement raw materials and incorporated in clinker product, whereas all cyanides are destroyed at the high temperatures of cement production [10]. The transformation of "unwanted" waste SPL into valuable feedstock for other industries, promotes the cross-industrial cooperation and a circular economy. In addition, due to the repurposing of SPL materials, there may be reductions in the environmental footprint of cement industry with respect to CO_2 and NOx [10].

2. SPL Management at Hirakud Smelter

Hirakud smelter had taken several strategic & sustainable initiatives adopting the 4R approach for SPL management. The practices followed at Hirakud smelter focus on protecting human health and the environment from impacts associated with generation, storage, handling, transportation and disposal of SPL. The first step is the layer-by-layer delining for effective segregation of SPL waste into different categories as per the end application or use. The last option is responsible disposable following the government regulatory norms with minimum impact on the environment and human health. Figure 2 shows the typical steps involved in segregating the SPL waste, after the pot has failed and stopped.

Figure 2. Typical processing steps after pot failure. Left: cavity cleaning after pots failure, Center: layer-by-layer delining for better segregation, Right: segregation of carbon & non-carbon portions of SPL.

The approach adopted by Hirakud smelter was to reduce the SPL generation by redesigning the cell lining while improving energy efficiency, performance and pot life significantly. This has eventually reduced the quantity of SPL generation per ton of Al produced. Following section explains the modification in cell lining and its impact on process performance.

1.1. Redesign of Pot Lining to Reduce SPL Generation

While redesigning the lining of a cell, its thermal balance needs to be analyzed critically with respect to isotherm location in the refractory. This would not only prolong the life of the cell but also improve its performance. A new lining design was developed to reduce the SPL generation by means of reducing the mass of lining materials used in a pot along with improving the thermal balance of pot. Typical heat loss distribution from a Hall Héroult cell is shown in Figure 3.

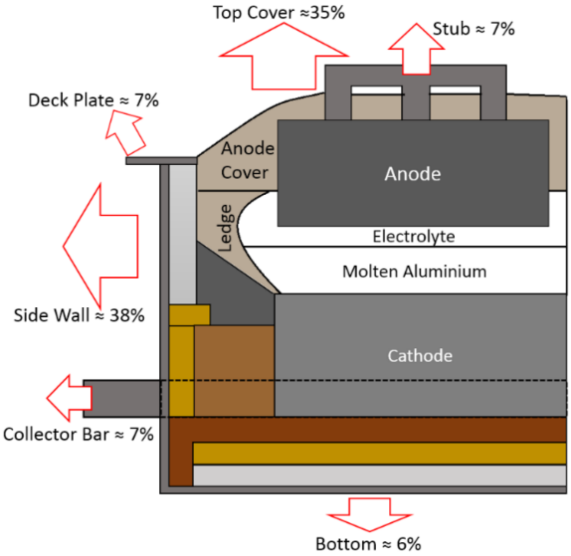

Figure 3. Typical heat loss distribution in an aluminium reduction cell.

Thermal balance of cell plays a critical role in defining ledge shape and its thickness. Improper heat loss distribution and process parameters may lead to freezing of the electrolyte on the cathode carbon surface with ledge toe extension under the shadow of anode as shown in Figure 4 (Left). The cathode temperature is also an important aspect for efficient cell operation, as cold cathodes can lead to formation of sludge/muck due to undissolved alumina as shown in the Figure 4 (Right).

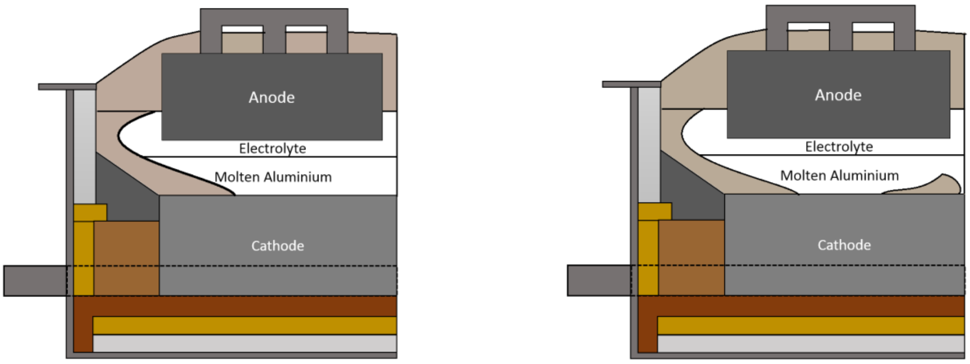

Figure 4. Impact of thermal imbalance. Left: ledge extended under the shadow of anode. Right: sludge formation over the cathode surface.

Ledge toe extension underneath anode or hard deposits on the cathode surface enhances the wear rate and chance of pothole formation, thus affecting pot life. Presence of extensive ledge and sludge can lead to an uneven current distribution in the cell, resulting in MHD instability, which adversely affects the cell operation and, consequently, requires higher anode-to-cathode distance (ACD) [14]. Hence, for efficient cell operation at minimum ACD, the cell lining design should ensure a nearly vertical ledge profile along with the isotherm location at an appropriate position in the refractory lining of the cell.

For this purpose, a thermo-electric model has been utilized to analyze the cell lining design and material modification. Additional information regarding thermo-electric model development for Hirakud 85 kA cell and its validation with industrial measurements can be found in literature [15]. In this study, simulations have been performed for analyzing changes in cell lining materials, lining design and CuCB. Desired thermal balance of the new cell was obtained after performing multiple simulations where the results yielded by proposed changes in design and materials were analyzed. The cell lining design has been modified around the cathode block, as shown in Figure 5, to alter the heat loss distribution from the cell for improving the thermal balance of the cell and electrolyte freezing isotherm placement in the refractory. The new lining design helped in attaining uniform current distribution, a nearly vertical freeze profile with a smaller toe and a thicker ledge at metal-bath interface, thereby providing energy saving as well as potential for improvement in pot life.

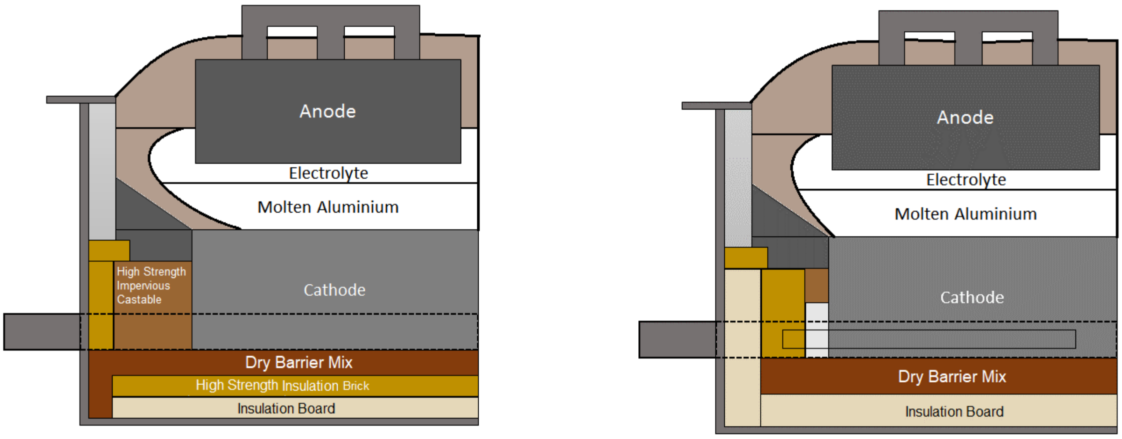

Figure 5. Typical modification in the cell lining design. Left: old lining design. Right: new lining design with CuCB.

This design modification was associated with changes in the quantities of lining materials. Table 2 shows the changes in the quantities of different lining materials for new cell lining design as compared to the old one, excluding the collector bars.

Table 2. Modification in cell lining materials quantities (in tonnes).

Cell Lining Materials	Old Lining design (t)	New Lining design (t)
First Cut Material	**Total = 8.60**	**Total = 7.80**
1. Cathode & tamping mix A	1. 6.20	1. 6.20
2. Carbonaceous groove mix-B	2. 0.40	2. 0.00
3. Carbonaceous seam mix	3. 2.00	3. 1.60
Second Cut Material	**Total = 12.47**	**Total = 10.41**
1. Dry barrier mix	1. 6.50	1. 5.50
2. High strength insulation bricks	2. 1.73	2. 0.16
3. Low strength insulation bricks	3. 0.12	3. 0.00
4. High strength impervious (castable)	4. 1.40	4. 0.40
5. Refractory brick	5. 0.27	5. 1.35
6. Insulation board	6. 0.27	6. 0.82
7. Remaining material unchanged	7. 2.18	7. 2.18

Figure 6 shows the improvement in ledge profile without ledge toe extension under the shadow of anode with new cell lining design along with CuCB. In addition, the simulation result shows reduction in the temperature gradient of the cathode block, along with increase in temperature of the corner cathode by about 50 ˚C. Overall increase in cathode temperature helped in reducing the chances of sludge formation thus improved the cell performance.

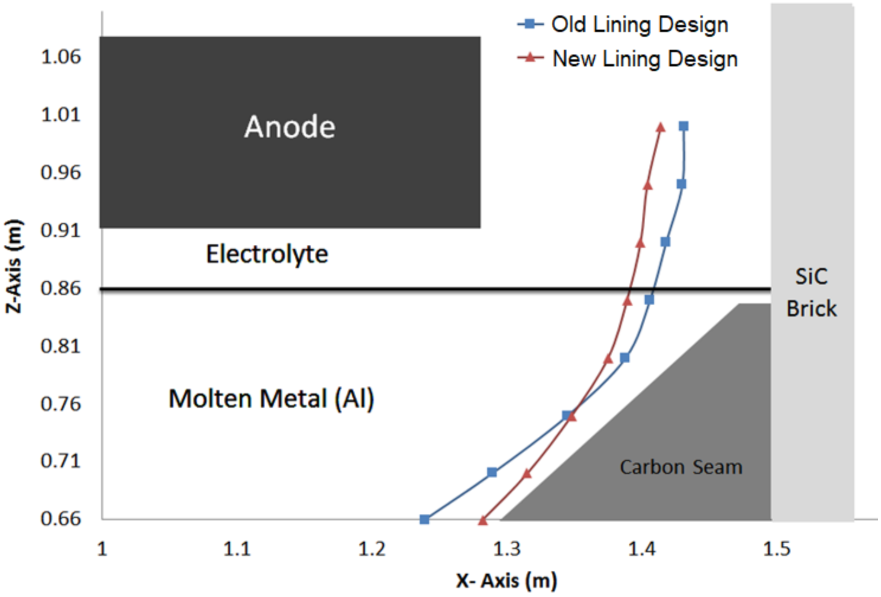

Figure 6. Improved ledge profile with new cell lining design.

The simulation analysis incorporating the CuCB helped improving the current distribution in cathode block, hinting towards a positive influence on pot life [4]. The simulation results also show that cell lining modification has improved the ledge profile as well as cathode temperature profile, which would improve the cell operating condition. Table 3 shows the performance comparison between old and new lining designs, where both a 2.1 % reduction in specific energy consumption as well as a 13.6 % increase in pot life have been effectively achieved.

Table 3. Comparison of pot performance.

	Old Lining Design	New Lining Design
Current (kA)	85	85
Pot net voltage, excluding line loss (V)	4.38	4.31
Current efficiency (%)	93.0	93.5
Cathode voltage drop (mV)	350	270
Pot specific energy consumption (kWh/t Al)	14 035	13 734
Pot life (days)	~ 1760	~ 2000

New design pots have been running efficiently over the period of last 5.5 years. The new lining design offers a reduction of about 3 tonne in the virgin lining materials (both carbon & non-carbon parts). However, the actual reduction in SPL quantity will be known only after completion of its operational life. Autopsy of an old design pot revealed that SPL quantity was increased by about 8–9 % compared to virgin material. Therefore, a similar increase in weight has been assumed for the new cell lining design in such a way that the new design potentially offers a reduction in the SPL generation from 20.41 kg/t Al to about 15.55 kg/t Al, or 23.8 %. Measurement of cathode surface wear was performed in new design pots and found that the erosion rate of cathodes is much smaller when compared to the old design pot. Based on this result, pot life is expected to exceed 2200 days, which would help in attaining a SPL generation of about 14.14 kg/t Al or a 30.7 % reduction with respect to the original figure.

1.2. Recycling of Pot Lining

On the recycling front, Hirakud smelter had been working to use the old lining material of prematurely failed or shunted pots when restarting these pots. There had been several instances of prolonged power outages, which had forced shunting of several pots. These pots were restarted after the complete normalization of the potline. Recently, in 2018 Hirakud smelter faced a prolonged power outage resulting in shunting of 66 pots. Similar power blackout situations had happened in the past, which led to many pots being shunted during 2012 and 2014. These situations had enabled the plant to develop and mastering the technique of restarting the pots with partial preheating, also known as crash start-up of pot.

The shunted pots were segregated and grouped as per their age as well as minor maintenance requirements. Subsequently, the pots were restarted in groups and preference was given to low age pots. The medium and high age pots were examined and minor repair work performed by replacing SiC block, carbon seams, etc., prior to restarting. This strategy of restarting the shunted pots was adopted to enhance the operational life of a particular pot, which resulted in reduced SPL generation per tonne of aluminium produced.

1.3. Recovering Energy from SPL

Apart from recycling, Hirakud smelter has been exploring ways to utilize the SPL in other industries such as coal-fired power plant. The trial was performed in a captive power plant using the first-cut material of SPL. This was performed by co-processing / incineration of SPL with limestone in the circulating fluidized bed combustion unit of power plant. Trial was conducted at 0.05 % SPL with feed rate of 11 kg/h and thereafter at 0.10 % with feed rate of 22 kg/h. Limestone was mixed with SPL in 1:1 ratio to absorb HF and SO_2 emissions. The particulate matter monitored during the trial was found to be less than 50 mg/Nm^3 and it varied from 36.2 mg/Nm^3 to 47.3 mg/Nm^3. On the other hand, SOx, NOx, HF were found to be below the norms set by the pollution regulatory bodies. During the trial cyanide was not observed in the stack emission. Though the results from the trial were deemed satisfactory, further extension of this approach would require consent from regulatory bodies.

1.4. Reuse of SPL as Raw Material

Hindalco smelters are also exploring options with the cement industry to reuse the SPL as raw materials. The SPL can be used in the different stages of cement manufacturing process as a raw material as well as an alternative fuel. This work is in the initial stages of development.

3. Conclusions

Spent pot lining is a hazardous waste and a major threat to the environment. It is being managed by Hirakud smelter by adopting 4R (Reduce, Recycle, Recover & Reuse) approach. This work majorly focuses on the first "R", i.e., redesign of pot lining to reduce the SPL generation. Pot lining was redesigned to improve the thermal balance, ledge profile and isotherm location in the refractory by modifying the lining design and materials along with Cu-insert collector bar. This has not only improved the pot performance with respect to the energy efficiency, but also improved the pot life. The new design pots are already running for the last 5.5 years and offering an extended pot life of more than 200 days along with reduction in lining material quantity by about 3 tonne as compared to old design. The new cell lining design reduces the SPL generation from 20.41 kg/t Al to about 15.55 kg/t Al, or 23.8 %. Based on cathode surface measurement, the pot life is expected to exceed 2200 days, which provides further reduction potential in SPL generation to about 14.14 kg/t Al or 30.7 % with respect to the original figure. Apart from the redesign approach, other avenues such as recycling and recover have also been tested while exploring the reuse of SPL with cement industries. These sustainable practices would help in reducing the SPL impact on the environment.

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