The LCL&L process: A sustainable Solution for the Treatment and Recycling of Spent Potlining.

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Abstract

Spent potlining (SPL) is a hazardous waste produced by aluminum smelters. SPL is generated from the internal lining of aluminum electrolysis cells, constituted of carbon and refractory bricks and replaced after five to eight years in service. It is classified as a hazardous waste because of its contamination with fluorides and cyanides and its reactivity with water, generating explosive gases. Nowadays, the aluminum industry has made some progress with the SPL issue by recognizing that landfilling is no longer acceptable by most local communities. In 2008, Rio Tinto Alcan inaugurated a new plant in Jonquière (Québec) for the treatment of 80 kt of SPL annually, based on the low-caustic leaching and liming process (LCL&L) developed at Arvida Research and Development Centre in the early 1990's. This paper describes LCL&L process, including valorization routes for its by-products and some technological challenges faced during the ramp-up of the plant to its nominal capacity.

Keywords: Spent potlining; LCL&L process; LCL&L by-product valorization.

1. Introduction

The aluminium smelting process takes place in a steel shell lined with refractory bricks and carbon cathodes. During the operation of the cells, molten fluoride salts and sodium penetrate into the carbon cathode lining and eventually into the alumina refractory lining or firebrick below. Pot failure occurs generally after five to eight years due to the thermo-mechanical stress generated within the pots, which allow attack of the iron collector bars and refractory lining by bath electrolyte or liquid aluminium. During pot shutdown, bath and liquid metal are siphoned off as much as possible. Once cooled, the remaining lining is then broken up and dug out of its steel shell. Iron and large aluminum pieces are sorted and recycled separately. The residual material is called spent potlining (SPL). Figure 1 shows the cross section of a pot. SPL is recognized as hazardous material because it contains significant concentrations of toxic and leachable constituents (cyanides and fluorides). Moreover, in contact with water, the reactive species of SPL, such as residual metallic Al, aluminium carbide and nitrides, have the potential of generating ammonia, hydrogen and methane. Hence, transportation, storage and final disposal of SPL are subject to strict environmental regulations.

Each ton of aluminium produced generates about 22 kg of SPL. Several factors can contribute to the variation in kg of SPL per ton of Al produced or to the variation in chemical composition of SPL. Electrolysis technology, pot operations, achieved lining life, and demolition/relining practices are the major factors. For example, the amount of bath and frozen aluminium that will remain inside the pot and thus in SPL depends on the dismantling procedures of the plant. The fluoride penetration inside the linings depends on the type of materials and the operation lifetime. For Rio Tinto (RT) in Québec, about 20 kt of SPL is generated per year.

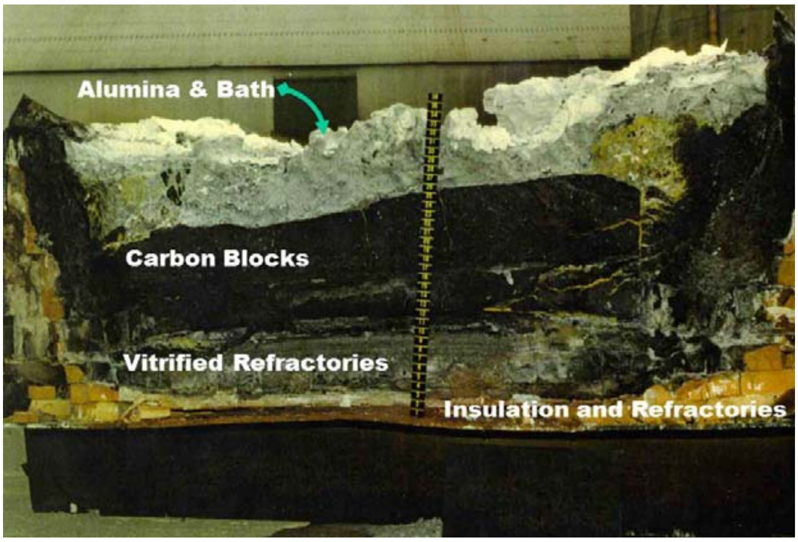

Figure 1. Cross section of an electrolysis pot.

Until mid 1980's, Rio Tinto (RT) operated in Jonquière (Québec, Canada) a plant treating SPL to produce cryolite. That plant was closed because of reduced cryolite consumption in smelters and, since then, RT has accumulated about 600 kt of SPL in safe dedicated storages. Today, less than 500 kt remain stored. Landfilling of SPL is not an option if the aluminium industry wants to claim an acceptable degree of sustainability. Several options to treat SPL exist and were reported in the literature [1, 2]. The biggest challenge for all these options for total recycling of SPL is coming from its heterogeneous composition and its high content in sodium and fluoride. Due to stricter environmental regulations in several places around the world, it becomes more difficult to send SPL without partial or total treatment directly to industries processing hazardous wastes (cement or steel industries).

In the early 1990s, RT developed at the Arvida Research and Development Centre (ARDC; Jonquière, QC) the hydrometallurgical process called LCL&L (Low Caustic Leaching and Liming), generating inert by-products with high potential for valorization [3,4]. In 2003, after a thorough evaluation of the various available alternatives, RT chose the LCL&L as the most sustainable solution for the treatment of its SPL. In 2008, RT built an 80-kilo tonnes per year (ktpy) SPL treatment plant in Jonquière (QC) based on this process [5]. This paper is an update of the experience acquired by RT since the plant's start-up [6], including ramp-up capacity, technology challenges that were overcome, and development of by-products valorization routes.

2. The LCL&L Process

2.1. Process description

The LCL&L process leaches fluorides and cyanides out of spent potlining (SPL) and generates inert by-products that can be valorized (Figure 2). The treatment is divided in two parts: one dry and one wet sectors. The dry sector includes unloading, handling and storage of SPL containers, SPL grinding (less than 300 microns) by an air swept autogenous mill with air classification and screening, and ground SPL storage. The wet sector consists first of leaching steps in series; the first leach is done with water to extract the water soluble fluorides and most of the cyanide compounds, followed by a low caustic leach to extract the remaining fluorides and cyanides. After filtration, hydrated lime may be added to the inert residues, also named carbonaceous by-product (CBP), to reduce if needed its content in leachable fluorides. Cyanide compounds (such as ferri-ferrocyanide complexes) contained in the leachate are destroyed in pressurized reactors by high temperature hydrolysis (180 °C). During cyanides destruction, particulate iron oxide is generated. If necessary, liquor after the flash tanks may need to be filtered to remove this colloidal iron. The resulting liquor is concentrated by evaporation in a multistage evaporation and crystallization circuit, generating caustic liquor at a high concentration compatible, for example, with operation of a Bayer alumina plant, while fluorides are precipitated as sodium fluoride. NaF is one of the by-products of the LCL&L process. After filtration, the solid sodium fluoride is re-dissolved in water and is reacted with lime to generate inert calcium fluoride pulp and low caustic solution. This caustic solution (causticized liquor) is recycled in the process at leaching, the excess returning to the evaporator to generate a concentrated caustic solution. Thus, the LCL&L process generates three by-products which can be valorized: carbonaceous by-product (CBP), fluoride by-product (FBP) in the form of either NaF or CaF_2, and a concentrated caustic solution (evaporated liquor).

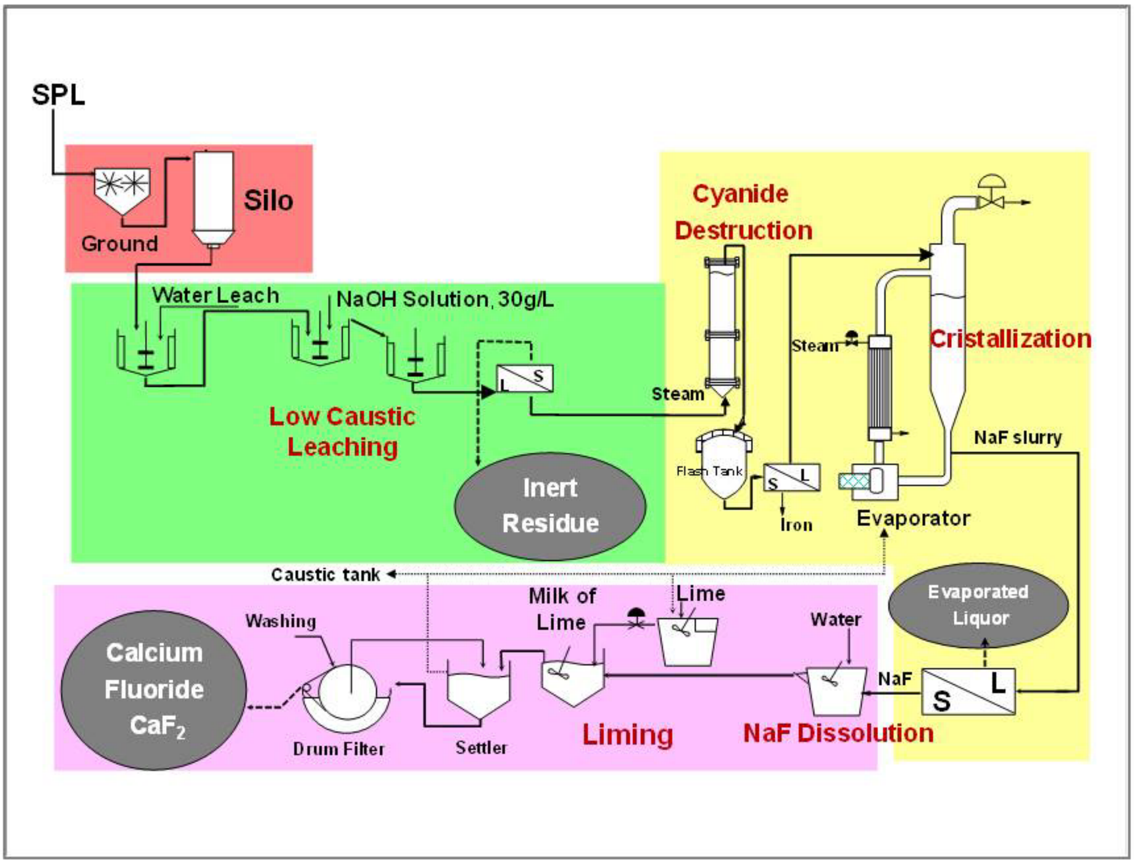

Figure 2. LCL&L process flow diagram.

2.2. Technology package and analytical methods

Pilot tests during the process development of the leach step and NaF caustification step were done at a scale of about 25 kg/h SPL at the Centre de Recherche Minérale (CRM). The nominal capacity of the plant built in 2008 is 10.7 t/h SPL, representing a significant up-scaling factor of 450. The basic information required to build the plant was transmitted to the Engineering via the Technology Package, including the Process Flow Diagram with each stream characteristics (flow, temperature, composition). The simulation software Aspen Plus® was used to obtain a detailed steady-state mass and energy balance of the process. All the information (including reaction conversions, SPL composition, compounds solubility) obtained since the start of the plant in mid-2008 was used to continuously improve the reliability of the Aspen model.

For process control, new analytical methods were developed by the ARDC analytical group to measure characteristics of the caustic liquors (fluoride, cyanides, caustic, alumina) or the by-products (pH, leachable fluoride or cyanide contents). Standard methods for measurement of leachable fluoride and cyanide involved delays of 24 hours, which is incompatible with efficient process control. New methods were developed to obtain equivalent measurement in one hour, and thus enabling operators to detect off-spec material generation and adjust production parameters. Development of new analytical methods was also done to determine a detailed composition of SPL (for different electrolysis technologies) and purity of carbonaceous and fluoride by-products.

2.3. Ramp-up

Because of the context of a new technology demonstration, a progressive ramp-up was needed before reaching the nominal plant capacity. The plant was started up in April 2008 and reached its full capacity in 2014 (Figure 3). The first years of operation have been dedicated to major equipment troubleshooting, process adjustments and optimization.

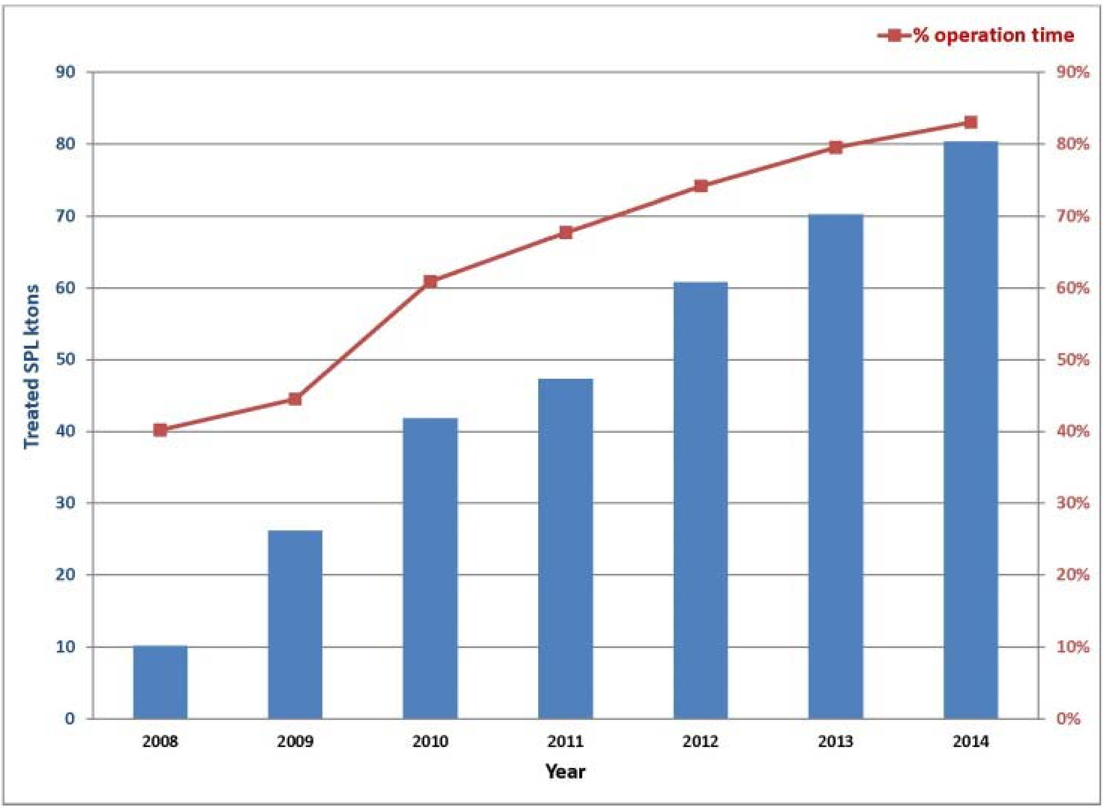

Figure 3. Plant capacity ramp-up.

Very early after the plant start-up, heavy scaling of the evaporator-crystallizer unit was experienced. Scale formed on the tube sheet at the exit of the first effect heat exchanger tubes and on the side wall of the evaporating tank, blocking the liquor flow and leading to frequent plant shutdowns. Fundamental causes for this scaling were investigated by the ARDC [7]. Scaling was minimized by modifying the operating parameters and by changing the internal caustic concentration profile within the four different evaporation effects. General control strategy of the wet sector is to keep liquor flow and concentration constant as much as possible. Liquor flow was established to treat the nominal SPL tonnage based on an average SPL composition. The actual SPL tonnage feeding the wet sector is controlled based on the fluoride concentration in solution after caustic leach, to be sure that this liquor is not supersaturated. The plant capacity is then lower if fluoride content in SPL increases, and vice-versa. Caustic concentration at caustic leach is controlled: it has to be high enough to ensure good fluorides extraction, but not too high to avoid fluoride solubility reduction at high caustic concentration which would reduce plant capacity.

Some modifications and simplifications were introduced to the leaching steps since the plant start-up and the initial LCL&L process [5]. Water leach filter, activation and polishing leach steps were by-passed. To improve the separation of solid and liquor, a settling tank was also installed after the leach reactors and before a belt filter. The objective of this decanter was to thicken the slurry out of the caustic leach reactors to reduce the size of the downstream caustic leach filter. Synthetic flocculent is injected to the decanter feed to form flocks and increase solids settling rate. Overflow of the decanter is pumped to the cyanide destruction unit feed tank. R&D was done in the last two years in order to find the best flocculent and to avoid solid accumulation and blockages of equipment in the cyanide destruction sector.

If required by local environment regulations, lime can be added to CBP to reduce its level of leachable fluorides as measured by TCLP procedure. However it must be recognized that lime addition will also increase the pH of CBP to pH ~ 13 that may be unacceptable depending on local environment rules. If required, it is possible the re-slurry with hot water the limed CBP, and then filter and wash it on a second filter, to remove the caustic generated by the lime and reduce the pH to a value around 12.5. Other additives were also tested and may be used as alternatives to lime addition with respect of low leachable fluoride content (< 150 ppm) and low pH (< 12.5) of CBP according to Quebec environment regulations.

The plant also faced safety challenges due to the reactivity of SPL with water. The heart of the LCL&L process is the leaching step. Agitated cascade reactors digest the slurry extracting fluorides, cyanides, sodium, alumina, and silica into the caustic liquor, and generating explosive gas. Any intercalated sodium and remaining aluminium metal will react with water and caustic to generate hydrogen:

$$2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2 \qquad (1)$$

$$2\ Al + 2\ NaOH + 2\ H_2O \rightarrow 2\ NaAlO_2 + 3\ H_2 \qquad (2)$$

Aluminium nitrides and carbides will generate ammonia and methane gas respectively:

$$AlN + NaOH + 2\ H_2O \rightarrow NaAlO_2 + NH_4OH \qquad (3)$$

$$Al_4C_3 + 4\ NaOH + 4\ H_2O \rightarrow 4\ NaAlO_2 + 3\ CH_4 \qquad (4)$$

To avoid accumulation of explosive gazes inside the leaching reactors, dilution air is provided inside the reactors. Continuous measurement of explosive gas on the vent outlet of the first leach reactor is also provided. Freshly ground SPL can also react with moisture to form a mixture of potentially explosive gases. For most of the SPL grinding sector, the risk of explosion has been eliminated by diluting the explosive gas mixture with air to a concentration inferior to 25 % of the lower explosion limit (LEL). However, inside the screw conveyors located underneath the silos, this strategy is not possible because the high air velocities would sweep all the material. Thus, nitrogen is injected downstream the silos to achieve partial or total inerting of the explosive gas mixture in the conveyors.

3. By-products Valorization

As mentioned previously, the plant is producing three main by-products: inert residues also named carbonaceous by-product (CBP), fluoride by-product (FBP) in the form of either NaF or CaF_2, and a concentrated caustic solution (evaporated liquor). In 2014, the plant treated 80 kt

SPL and produced 94 kt of CBP, 48 kt of CaF_2 and sent 30 kt of caustic solution (27 % NaOH) to the nearby Vaudreuil alumina plant.

3.1. Mixed carbonaceous by-product (CBP)

As mentioned in [2], cement industry and few other industrial pyrometallurgical processes are capable of using the SPL as generated, without any pre-treatment. However, strict restrictions on the sodium and fluoride content in the final product limit the amount of SPL that can be added to these processes. Nowadays, environmental regulations are also stricter and it becomes difficult for these industries to accept unprocessed SPL.

Since 2006, RT has developed an intensive R&D program for valorization alternatives for the CBP. Since the plant treats all of the SPL (both carbon lining and the refractory lining), the CBP contains approximatively 30 – 40 % carbon (on dry basis) and 60-70% of inert materials (mostly SiO_2 and Al_2O_3). Because of its mixed nature, CBP is essentially limited to be used as alternative fuel and raw material for clinker production in the cement industry. Compared to direct SPL valorization in the cement industry, the CBP contains five times less total fluorides and alkalis (sodium), which enables higher dosage into the kiln. The carbon is attractive for its energy content (approx. 13 GJ/t), while the inert material is attractive for its mineral composition (ash) relative to clinker chemistry. Moreover, residual inert fluorides (mostly in the CaF_2 form) in the CBP have the advantage of lowering the energy required to produce clinker due to its fluxing properties. However the mixed nature challenges state of the art clinker production, since minerals are normally fed to the kiln at the cold end while solid fuel is fed to the hot end. Plant scale tests done in 2009 at the Holcim cement facility located in Joliette, Québec, indicated that nearly 20 % of the total CBP production could be valorized this way. The use of CBP by a cement plant allows total recovery of the carbon energy value and of the mineral content of CBP, it has no impact on clinker mineralogy and on cement quality, and does not create any significant environmental concern.

Another option identified to valorize mixed CBP is to burn the low sulphur carbon (around 0.1 % S) to recover its energy content. The remaining ash could be valorized as raw material for cement plants or in the refractory industry [8].

Since 2013, mixed CBP production has been valorized as low density (1250 kg/m^3) civil engineering construction material at Rio Tinto bauxite residue disposal site. While compacted to its maximum density, CBP has proven to be a very good geotechnical construction material.

3.2. CBP valorization with carbon and refractory brick separation

As a promising solution to valorize mixed CBP, carbon separation techniques, such as flotation, were tested in laboratory and in pilot trials. Carbon concentrate grade over 90 % C, with carbon recovery up to 95 %, and brick concentrate containing less than 5 % C were generated. In 2011, more than 150 t of CBP (dry basis) were successfully treated in a pilot unit to produce 50 t of carbon concentrate and 100 t of brick concentrate. The carbon concentrate has promising valorization options for the cement and steel industry, but has also an interesting graphitic value. In 2012-2013, 150 t of anodes containing 1% of this carbon concentrate were produced and successfully tested in electrolysis cells at Grande-Baie plant (UGB), Québec.

In the eventuality that the first cut (fraction of SPL above the collector bars, mainly carbon) and second cut (fraction of SPL below the collector bars, mainly refractory brick) would be separated during dismantling of the electrolysis pots, and then treated separately by the LCL&L process, it would be also possible to obtain separate carbon and brick concentrate. An R&D

project is on-going at the plant to test this option: a few hundred tonnes of each cut were recently treated separately with success at the plant. The processed brick concentrate contains around 5 % C (similar to results obtained by flotation) while the carbon concentrate contains above 80 % C. This option seems to be really interesting for valorization of fresh SPL.

3.3. Fluoride by-product (FBP) valorization

The valorization of the fluorides extracted from the SPL must take into account characteristics and quality constraints of the local market. In Quebec, because of the limited market for sodium fluoride (NaF), it is better to convert NaF to calcium fluoride (CaF_2), which has also the advantage of being inert. In Jonquière, the conversion to CaF_2 allows the FBP to be used as an alternative raw material in the nearby aluminium fluoride plant, allowing a considerable saving. At its nominal production, the fluoride plant is consuming 90 ktpy of fluorspar (mineral CaF_2) to produce aluminium fluoride, AlF_3 in a two-step process: the first step being the generation of HF by reacting CaF_2 with sulphuric acid while the second step is the production of AlF_3 by reacting anhydrous HF with aluminium hydroxide ($Al(OH)_3$). AlF_3 is then re-used in the electrolysis smelters as an important additive for the bath, allowing closing the loop of the fluorides. In order to replace fluorspar by LCL&L CaF_2 for AlF_3 production, R&D was done in recent years to improve the quality of FBP to meet the AlF_3 plant requirements. The CaF_2 produced by causticizing NaF with lime in water must contain as little as possible hydroxide and oxide compounds. Indeed, these compounds would later consume sulphuric acid at the fluoride plant, producing unexpected water in the process that must be controlled by addition of oleum. Other impurities in the CaF_2 could also decrease the quality of the produced AlF_3. The other challenge for the CaF_2, in addition to its purity, is the particle size necessary for its introduction at the fluoride plant (around 50 µm). As the LCL&L plant is producing CaF_2 paste with small particle size around 5 - 10 µm and with approximatively 45 wt. % moisture content, the paste must be dried and calcined at high temperature (700 – 800 °C) for sintering/agglomeration.

During the last two years, R&D efforts were focused on both chemistry and transformation of CaF_2. With better control of lime addition and process parameters, side reactions of lime with sodium carbonate or with aluminate and silicate in solution were minimized, avoiding large precipitation of these calcium salts with CaF_2. Pyroprocessing test in rotary kiln also resulted in CaF_2 particles enlargement. The result of these efforts was completed by a pilot trial producing 2000 t of CaF_2 pulp with good purity (87 dry wt.% CaF_2). This pulp was then processed at high temperature in a rotary kiln, and the particle size specification for the dry material target was reached. The final CaF_2 was then introduced at the fluoride plant for several weeks, replacing successfully 25 – 30 % fluorspar feeding with minimal process modifications, and allowing for a full qualification of this valorisation route. Future works will include the engineering of a full scale transformation process (sintering/grinding) in order to close the fluoride loop of the LCL&L process.

4. Conclusion

The LCL&L process was developed by Rio Tinto to treat spent potlining generated by aluminium electrolysis cells. It is a proven technology with an 80 kt plant in constant operation. The capex and cost per ton of the process is relatively high, however it is a good alternative in situations when transportation costs to cement plants are high or not feasible due to legal compliance requirements.

Meanwhile, R&D was done to develop and implement the valorization routes of the LCL&L by-products. We succeeded to close the loop of the fluorides with the use of CaF_2 by-products at the fluoride plant, making the LCL&L process a sustainable and economical option to efficiently treat SPL. This plant is an interesting option for other aluminium producers in Quebec and in North America for the disposal of SPL. The LCL&L process should also be foreseen as a commercially available technology solution for application in other regions of the world where a significant amount of SPL needs to be managed.

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