Treatment and Valorisation of Solid Wastes from Smelters with the Low-Caustic Leaching and Liming Process

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Abstract

Spent pot lining (SPL) is a hazardous waste generated from the internal lining of aluminum electrolysis pots consisting of carbon and refractory bricks. This residue is classified as a dangerous waste mainly because of its contamination by fluorides and cyanides, and its reactivity with water, generating explosive gases. In 2008, Rio Tinto inaugurated a new plant in Jonquière, Québec, for the treatment of spent pot lining. This plant is based on the "Low-Caustic Leaching and Liming" process (LCL&L) developed at the Rio Tinto Arvida Research and Development Centre (ARDC). This hydrometallurgical treatment detoxifies SPL and produces inert by-products, which are then used as raw materials in different industries such as the cement industry.

In the last decades, Rio Tinto operations in Québec accumulated about 20 kt of alumina contaminated with electrolytic bath and other impurities. Due to its higher content in impurities (Si, Fe and P) and constraints in product quality, re-use of this alumina in aluminum electrolysis is limited and other solutions are sought. Insertion of this material at the SPL treatment plant was studied by ARDC. It was demonstrated that the hazardous properties of the contaminated alumina (mainly leachable fluoride) can be removed by the LCL&L process and that the content in alumina of the inert by-product can thus be improved. This alumina beneficiation in the by-product of the SPL treatment helps for its valorization in cement plant.

This paper describes the LCL&L process characteristics, including valorization routes for its by-products, and the proof of concept and pilot test done for the insertion of contaminated alumina.

Keywords: Spent pot lining, LCL&L process, Waste valorisation.

1. Introduction

In 2020, approximately 1.45 Mt of Spent Pot Lining (SPL), also known as Spent Cell Lining (SCL) or "Brasques Usées" in French, were generated from the production of primary aluminium according to the International Aluminium Institute [1]. It is the most significant solid waste stream from the aluminium electrolysis process and the second one from the aluminium industry after bauxite residue (approximately 160 Mt of dry residue in 2019). The amount of SPL generated to produce one tonne of aluminium will vary from one technology to another, the most recent technology being the most sustainable one (about 20 kg SPL/t Al).

SPL is the solid cathodic waste product generated during the production of primary aluminium. The lining of the pot is typically made of two layers, an insulating refractory lining and an interior carbon lining. During the life of the cell, the carbon cathode material is continuously impregnated by the chemical components of the bath and the components coming from the electrolysis reaction. One of the main causes for electrolysis cell end of life is when liquid aluminium and bath pass through the cathode and reach the steel bars or the pot shell. At the end of its life, the electrolysis pot must be shut down and rebuilt. After removing as much bath and metal as possible and separating the cathode bars from the rest, materials left over are the SPL. SPL includes both a carbonaceous fraction (first cut) and a refractory fraction (second cut) as well as entrained cell electrolyte, alumina crust, metallic aluminium particles and the mineral phases created by fluoride and sodium attack of the refractories. Some smelters keep the first (1st) and second (2nd) cut SPL separate, others do not, and the SPL is removed as one 'cut'.

SPL is recognized as hazardous material. The disposal and/or processing of SPL is complicated by the presence of reactive metals and toxic substances such as cyanides, nitrides, carbides and fluorides salts. In contact with water, SPL emits hydrogen, methane and ammonia. The historical solution to dispose of SPL was landfilling close to smelters. Even if this solution does not correspond today to environmental and regulatory considerations in most countries, it is estimated that more than 50 % of SPL generated annually is stockpiled or landfilled. Other options for managing SPL include treatment and use in other industries, either as a direct feedstock material or fuel, for example in cement or steel production. The classification of SPL as a hazardous waste also makes it subject specific to The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal. Thus, the transport of SPL across borders is highly regulated in most jurisdictions.

1.1 LCL&L Process

All the SPL generated by Rio Tinto in Canada is treated and valorised by the SPL treatment plant in Saguenay, based on the LCL&L (Low Caustic Leaching and Liming) process. This hydrometallurgical treatment removes hazardous properties of SPL by leaching fluorides and cyanide compounds out of SPL and removing hydroreactivity of SPL, thus generating inert by-products that can be more easily valorised. This process has been developed by the Rio Tinto Arvida Research and Development Centre (ARDC), in Quebec, since the 90s. It was developed to process SPL from old storages and fresh SPL from operating smelters. It can also process SPL cuts individually or mixed SPL.

As shown in Figure 1, the main steps of the LCL&L process are:

- SPL crushing, grinding and sizing,
- Low caustic leaching,
- High-pressure cyanide destruction,
- Evaporation to separate fluoride from high caustic solution,
- Calcium fluoride precipitation by liming.

The LCL&L process has been industrialized in the SPL treatment plant in Quebec. This plant was started up in April 2008 and reached its full capacity in 2014. Due to the demonstration context of a new technology, a progressive ramp-up strategy was needed before reaching the nominal plant capacity (80 kt/a). Through ongoing R&D work on the LCL&L process, major improvements were made to the SPL treatment plant in 2018 to provide a more energy-efficient process and facilitate inert by-product valorisation. More details on these process changes can be found in [2].

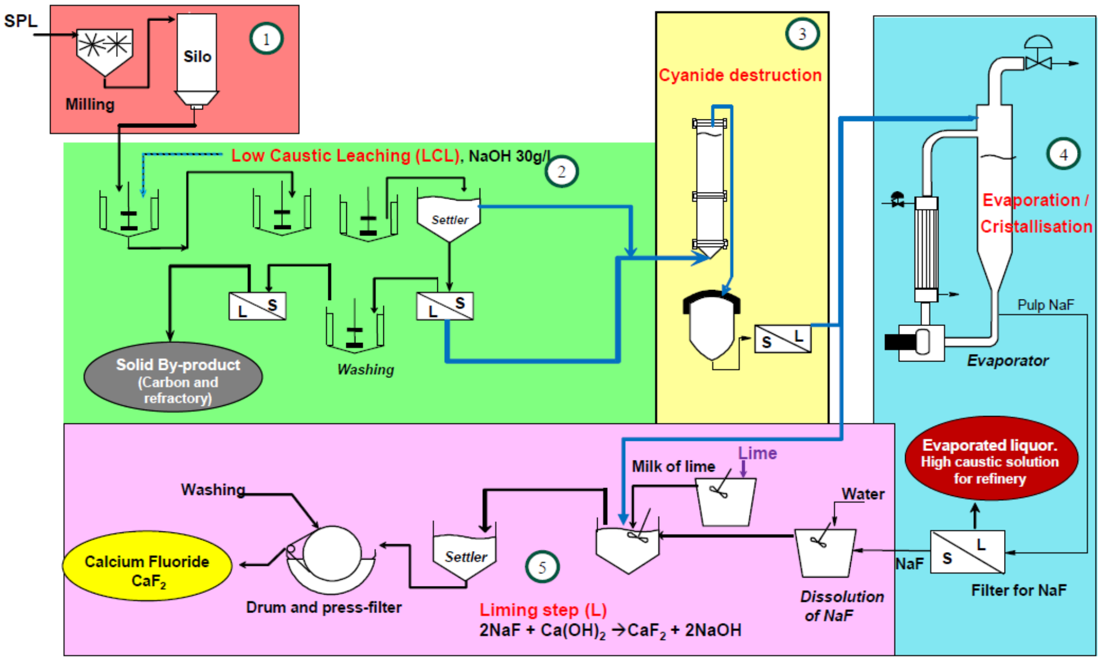

Figure 1. Flowsheet of the new LCL&L process implemented in 2018.

1.2 Valorisation of the LCL&L By-Products

The cement industry as well as some other industrial pyrometallurgical processes can use SPL as generated, without any pretreatment [3,4]. 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, Rio Tinto has developed an intensive R&D program to find valorisation alternatives for the LCL&L by-products. Due to its mixed nature (carbon and refractory compounds), the treated SPL is essentially limited to be used as alternative fuel and raw material for clinker production in the cement industry. Compared to the direct valorisation of SPL in the cement industry, LCL&L treated SPL contains ten times less total fluorides and lower alkalis (sodium), which enables a higher dosage in 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), which is very similar to that of clinker chemistry. Moreover, residual inert fluorides (mostly in the CaF_2 form) have the advantage of lowering the energy required to produce clinker due to its fluxing properties. However, due to its mixed nature, it challenges the state-of-the-art clinker production since minerals are normally fed to the kiln at the cold end while solid fuel is fed at the hot end.

Depending on the use of the material in the cement process, it is more interesting to separate the carbon fraction from the refractory fraction. The first cut (SPL fraction above the collector bars, mainly carbon) and the second cut (SPL fraction below the collector bars, mainly refractory brick) can be separated when dismantling the electrolysis pots. Improvements to the SPL treatment plant were also performed in the last years, enabling the LCL&L process to be fed either by mixed, first or second cut SPL, depending on the targeted market (geotechnical, energy or raw material for cement plants). Several thousand tonnes of each cut have recently been successfully treated at the plant. This has resulted in separate carbon and refractory concentrates with a very low fluoride content compared to untreated SPL. The carbon concentrate from the first cut treatment is called LCLL graphite, and the refractory concentrate from the second cut treatment is called LCLL ash (Carbon content < 10 %).

LCLL graphite is attractive for its energy content or its graphitic value. By adding carbon fines coming from anode residues to LCLL graphite, it is also possible to increase the carbon content (to about 80-85 %) and thus the energy value of the by-product. This mix is called LCLL fuel.

LCLL ash is attractive for the clinker chemistry due to its mineral composition and can be used as a raw material. In order to meet the various cement needs, the LCLL ash chemical composition was adapted by addition of alumina or refractory waste materials coming from the aluminium industry. This work was done in collaboration with cement producers and leads us to also develop new manufactured products based on treated mixed SPL and other industrial wastes as sources of silica or iron to meet customer needs.

1.3 Alumina Contaminated with Electrolytic Bath

Mixed alumina and bath materials such as what is reclaimed from floor sweepings, the cleaning of pot trenches or basements, is similar to the composition of anode covering material in Al_2O_3 content, but higher in impurities of silicon, calcium and general debris as shown in Figure 2 and Table 1. The market possibilities for this kind of mixed material are low and only feasible when transportation and labour costs are low and/or when there is some strong need to reclaim this type of material. Accumulations of any of these materials will create piles of “stranded value” of alumina content, fluoride equivalent content, and bath that may be able to be used or sold if it were in its pure form.

Due to its higher content in impurities (Si, Fe and P) and constraints in product quality, re-use of this material in aluminum electrolysis by Rio Tinto’s smelters in Quebec is limited and other solutions are sought. In the last decades, about 20 kt of this material was accumulated inside a shed.

Table 1. Composition of the alumina contaminated with electrolytic bath.

	Min (% wt)	Max (% wt)	Average (% wt)
Al_2O_3	59.0	85.0	69.0
SiO_2	0.5	1.4	0.9
Fe_2O_3	0.4	1.4	0.8
CaO	1.0	2.5	1.9
MgO	0.1	0.6	0.2
Na_2O	3.6	11.2	8.3
P_2O_5	0.01	0.03	0.02
Cl	0.02	0.03	0.03
S	0.2	0.4	0.3
F	6.0	25.0	15.0

Figure 2. Picture of the debris in contaminated alumina.

1.4 Objectives

However, due to its high alumina content, this contaminated material is of interest for boosting the quality of LCL&L by-products intended for the cement manufacturers' market.
As mentioned previously, in order to meet the various cement needs, the LCLL ash chemical composition was adapted by addition of alumina or refractory waste materials. Because bath contaminated alumina contains a lot of fluorine and sodium, it cannot be mixed directly with the byproducts of SPL treatment plant. The idea is rather to mix this material with SPL for treatment via the LCL&L process. The intention is to leach the fluorine and recover as much alumina as possible in solid form with the refractory by-products produced by the plant. We thus hope to observe an increase in the alumina content while keeping the fluorine and Na levels unchanged.

2. Proof of Concept

The SPL already contains electrolysis bath (cryolite and alumina), but a considerable addition of contaminated fine material could have impacts on the LCL&L process. The main risks to be studied were:

- Hydroreactivity of contaminated material and its impact on current controls in place at the plant (ventilation or nitrogen insertion).
- Presence of fluorine in the material. Could there be an impact on the residence time and the quality of the by-products? In addition, to control the fluorine precipitation chemistry in the evaporators, a fluorine target in g/L in the liquor must be achieved after leaching of SPL.
- Very fine grain size of the material compared to SPL. This can lead to dust issues when inserting the material into the equipment at the plant, but also to caustic leaching process issues, particularly for the wettability of the material, compatibility with flocculants for the decantation stage, and challenges during filtration of refractory by-products.
- Quality of final by-product: what is the recovery rate on the contaminated alumina added SPL? Is there an increase in % Al_2O_3 in the final by-product?
- Quality of evaporated liquor: as shown in Figure 1, one of the by-products is evaporated liquor which is reused by the neighboring refinery. Does the insertion of contaminated alumina impact the quality of this liquor which is used to wash the scaled tanks of the Bayer process?

A proof of concept was first carried out in the laboratory to validate the impact on different parts of the process. The load of leachable F by the LCLL process was tested and compared with that from a standard SPL. As shown in Table 2, the pure material compared to SPL has an impact on the process parameters at the leaching step. The fluoride in the leached liquor reaches 11.4 g/L which is slightly higher than the process target of 10.5 g/L to ensure proper decontamination.

Moreover, the higher bath content tends to dissolve more aluminum during the leaching step which increases the ratio Alumina/Caustic (ratio A/C), a key indicator of the liquor quality. As a result, the quality of the final product did not meet the established criteria for leached LCLL material.

Table 2. Results of the leaching tests done with contaminated alumina in LCL&L process conditions.

Feed	Leachate		Final LCLL material		
Contaminated alumina sample	Fluoride at leaching step	Ratio alumina/caustic	Al_2O_3	Na_2O	F
	g/L		% w/w	% w/w	% w/w
#1	10.7	0.51	76.2	2.8	5.9
#2	11.2	0.51	75.3	4.3	7.3
#3	11.1	0.55	77.9	3.4	6.7
#4	11.0	0.57	75.1	5.1	9
#5	11.4	0.56	66.6	6.9	10.9
#6	11.0	0.61	58.9	11.1	15.3
Target with SPL	10.5	0.35	> 25	< 6	< 4

Those tests indicated that contaminated alumina could not be used as is in the LCL&L process, and there is quite a large variation of fluoride content upon initial samples which impacts final product quality. Following those initial results a co-dosage strategy was tested in the same conditions. Mix of 50 % contaminated alumina over SPL indicated fluoride content at leaching step would respect the process target of 10.5 g/L. However, to account for the nonhomogeneous properties of the material, the subsequent tests were performed at a 10 % co-dosing strategy. This substitution rate was chosen to limit process impacts in case of further scale up while allowing increase of alumina content in the final LCLL material.

Table 3 and Table 4 summarize leaching tests performed on SPL and on a blend of SPL with contaminated alumina. Leachate and final LCLL material were analyzed to compare contamination profile of using the alumina. For those tests, 2^{nd} cut SPL and mixed SPL were used as well as different contaminated alumina lots with initial fluoride contents ranging from 17 to 25 % w/w. The results indicate that there was no significant degradation on either liquor or the final LCLL material. The sulfate contamination was higher with addition of contaminated alumina but not of concern for the process. For some mixed samples, fluorides were higher than SPL due to the initial content of the alumina and this will imply quality control before any piloting operation. On top of the presented contaminants, organic contaminations were also verified to ensure compliance with liquor specifications. The properties of the final material are of interest as an increase of the alumina content of approximately 20 % in the final product was observed while keeping fluoride and sodium content at relatively same level. The removal efficiency of fluoride is similar for mixed material and SPL which indicates compatibility of the mixed material to the LCL&L process conditions at this addition rate. Finally, the measured aluminum recovery was improved for the mixed material which is a value added for the final product.

Table 3. Composition of the leachate obtained for SPL alone and for SPL mixed with 10 % contaminated alumina.

Feed	Leachate	F	Cl	SO_4	Al	P	Si
		g/L	mg/L	mg/L	g/L	mg/L	mg/L
SPL with 10 % alumina	Average	10.4	64	2.7	2.3	4	282
	Range	8.5–12.0	54–75	1.5–5.1	1.7–2.9	4	153–360
SPL	Average	10.0	50	1.8	2.2	4	303
	Range	9.0–11.0	25–66	1.4–2.5	1.7–2.8	4	200–400

Table 4. Composition of the solid after LCLL leaching tests of SPL alone and SPL mixed with 10 % contaminated alumina.

Feed	Product	Al_2O_3	Na_2O	F	Al Recovery	F removal efficiency
		% w/w	% w/w	% w/w	%	%
SPL with 10 % alumina	Average	30.3	8.0	1.5	83.7	88.9
	Min	28.8	5.3	1.3	77.1	87.6
	Max	32.4	9.0	1.9	87.0	90.0
SPL	Average	24.9	7.8	1.5	76.5	88.4
	Min	23.1	5.5	1.1	70.7	85.5
	Max	26.7	9.2	2.0	80.9	90.6

Hydroreactivity measurements of contaminated alumina were made under the caustic leaching conditions of the LCL&L process. Figure 3 shows the cumulative quantities of gas generated over 1 hour. It shows that the evolution rate is similar or even lower for contaminated alumina than for SPL.

Contaminated alumina is a very fine material with a grain size of distribution of 80 % lower than 120 µm. Settling tests were carried out to validate the impact of substituting 10 to 20 % of SPL with contaminated alumina. These tests were carried out in comparison with standard SPL and under experimental conditions close to those of the plant. The results of the sedimentation rate, presented in Figure 4, show higher rates with the use of contaminated alumina than without. Moreover, the clarity of the overflow and the compaction of the underflow were not impacted by this substitution of SPL with alumina. Other process parameters, like filterability and wettability were also tested before proceeding to the following steps.

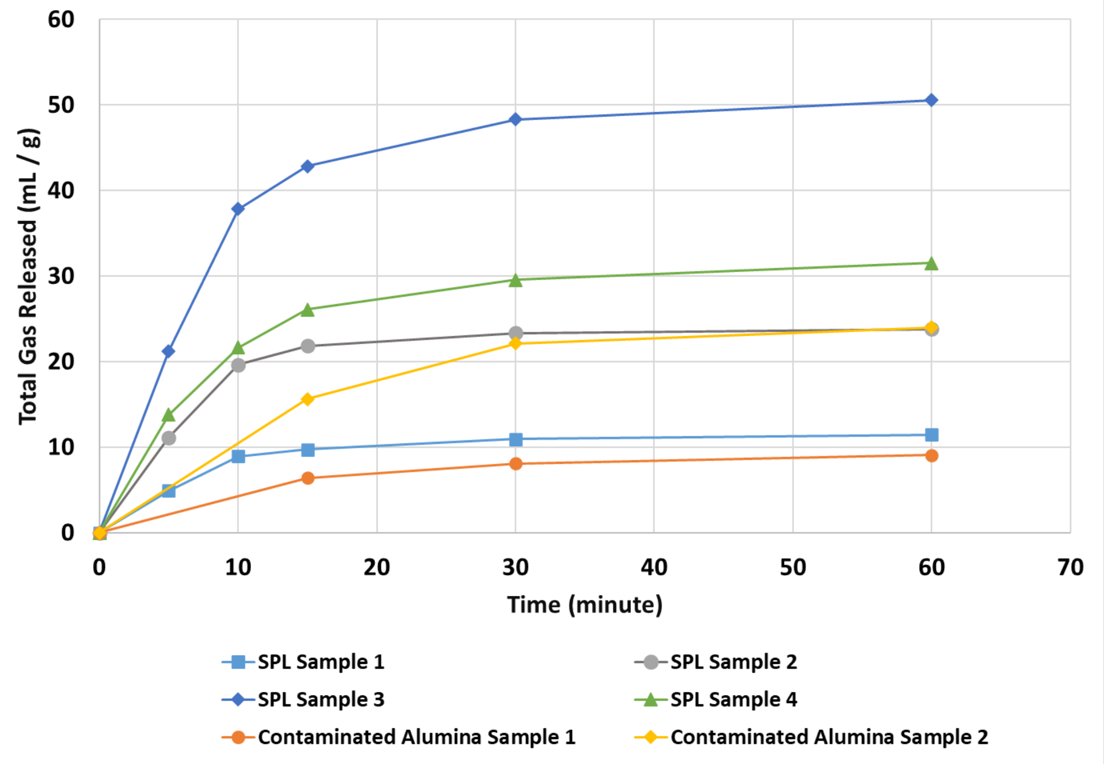

Figure 3. Rate of gas evolution from SPL and contaminated alumina with LCL&L leaching conditions.

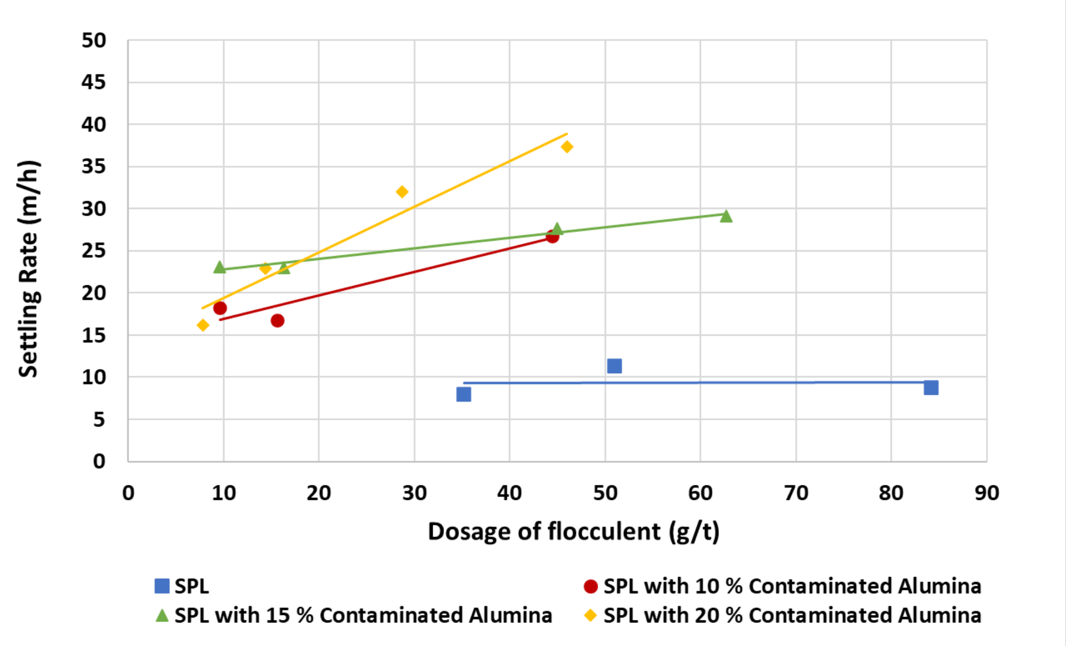

Figure 4. Settling rate of mixed material at different flocculent dosage.

3. Pilot Test at the SPL Treatment Plant

Since laboratory evaluation was conclusive it was decided to proceed with a pilot test. The pilot objectives were to confirm the impacts of doping SPL with contaminated alumina at the SPL treatment plant and to improve the alumina content of the final product by 20 % without increasing sodium and fluoride. Precautions were set-up to minimize negative consequences on the LCL&L

process for the pilot test. Hence quality control of the raw material was put in place to minimize high fluoride and other contaminants in the process. Also, the contaminated alumina was sieved to avoid introduction of undesirable materials that can be found in a waste warehouse (wood, brick, plastic). No modification of the process was necessary to perform the pilot test. Three operational days were considered sufficient to verify the pilot objectives. Considering the small particle size of the contaminated alumina compared to the usual SPL, few process adjustments related to process air flow were necessary to avoid blockage. At the plant, the material is fed into the leaching reactors by using conveyors without any flowmeter. Since controlling the feeding rate of the contaminated alumina was critical to meet the pilot objectives, a special dosing chart was put in place, coming from actual dropping test made for the SPL conveyors and adapted for the contaminated alumina density. A mitigation program, including a complete sampling program, a process control charter with several key performance indicators (KPI) and an inspection plan, was put in place at every step of the process. Among the KPI, pumps and grinder amperages, liquor temperature, filter pressure and vacuum, and decanter rake torque were monitored.

Co-dosing of more than 70 t of contaminated alumina with 800 t of SPL was achieved during this pilot test at the treatment plant. No adverse impact, or breakage, on the LCL&L process has been observed during the pilot test. Since the process parameters were under control and stable during the pilot, it was possible to modify the contaminated alumina feeding rate. Hence, the feeding blend varied from 5 to approximately 20 % alumina content during the campaign. According to the results there is potential for future optimization since the fluoride content of the leachate was still in the lower range of the process specification.

Figure 5 shows variations in final product quality during the pilot campaign. Hence, a 12 % increase was observed for the alumina content, as sodium content increases by 1 %. The total and leachable fluoride decreased by 12 % and 17 % respectively. In overall, the aluminum recovery for the campaign was estimated at 90%, which confirms laboratory test results. The leachate composition stayed within the KPIs during the campaign. Phosphorus, silicium and organic carbon were stable, but sulfate, chloride and alumina caustic ratio were in a slight increasing trend.

The following conclusions apply to the production of the pilot:

- Control of fluorine concentration: Stable fluorine in leachate with no major variation, in the lower limit of process targets (9 g/L) indicating potential for dosage modulation.
- Solid-liquid separation: The solid content in the settling tank overflow remained stable while no blockages or loss of equipment were observed during the test period.
- Process safety: No increase in LEL (Lower explosive limit) observed during the pilot which would have been attributable to contaminated alumina.
- Material insertion system: Although the selected method works for the targeted quantity, it was found not suitable for long-term operations.
- No impact on maintenance of filtration equipment.
- No accumulation of material in pipes and fans.
- 12 % increase in alumina content for the leached mixed material with almost stable sodium and decrease in fluoride.

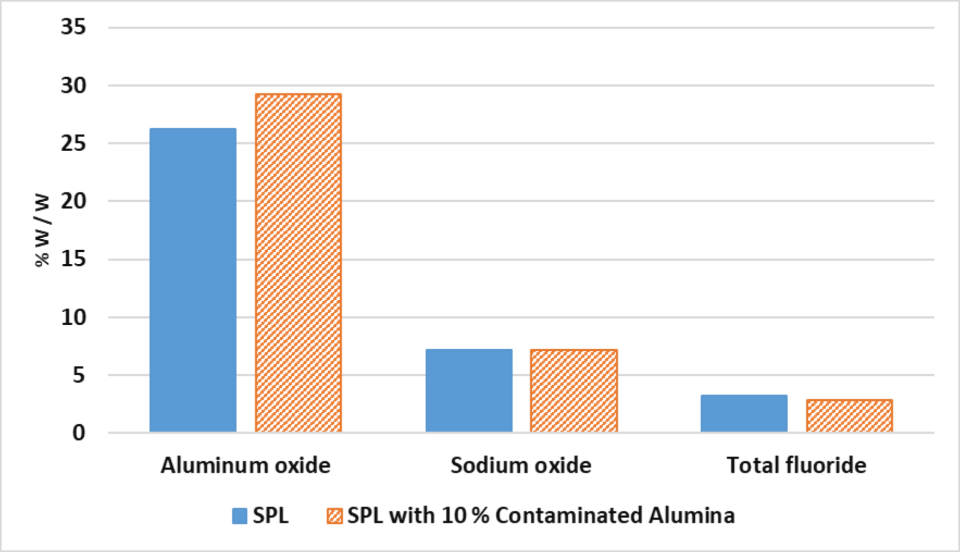

Figure 5. Average composition of the solid by-product achieved during pilot test with SPL only, and SPL mixed with 10 % contaminated alumina.

4. Conclusions and Next Steps

The LCL&L process was developed to treat fresh and stored spent pot lining (SPL), to remove hazardous properties of SPL and to transform it into valuable by-products. This work showed that it can also treat another separate waste and use its alumina content to increase the quality of the by-product used by cement plants. This represents another option of circular economy whenever aluminum smelters would struggle with the reinsertion in their process of alumina contaminated with bath.

In regard of the obtained results, the objectives of the pilot test were met. It was demonstrated that the co-dosing of contaminated alumina with SPL is a feasible option for the LCL&L process and can be operated at the SPL treatment plant. This represents an interesting opportunity to decontaminate alumina while increasing the alumina content of the final product from SPL treatment, which is advantageous for its valorization as raw material for cement plants.

As future steps, Rio Tinto is looking to perform a scale-up of the solution. This scale up would allow to evaluate mid-term impact of contaminated alumina addition with SPL, like sulfate and chloride content as well as alumina caustic ratio trend in the leachate. At the same time, diverse types of SPL would be tested and contaminated alumina variability would be more knowledgeable.

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