Fundamentals of Managing Spent Potlining (SPL)

Stephan Broek[1] and Harald Arnljot Øye[2]

1. Director, Environmental Engineering & Technology, Aluminium, Hatch Ltd., Mississauga, Ontario, Canada
2. Professor, Norwegian University of Science and Technology NTNU, Trondheim, Norway

Corresponding author: Stephan.Broek@Hatch.com

Abstract

As of recent, there is a renewed interest in the activities around the management, handling and treatment of spent potlining, or SPL. In this article the authors have combined their knowledge about the subject of SPL into a single publication in an effort to provide a most comprehensive review of modern methods of management and treatment of SPL globally.

The article starts with providing the essential characteristics of SPL that are important for the storage and handling of the material. Too often engineers must guess these characteristics and in this article these are summarized for reference. Following that, the article then goes into details on the various modern treatment methods that are applied in different regions of the world. In close, some new developments or initiatives will be discussed.

Keywords: Primary aluminium, spent potlining, waste management, handling, storage.

1. Introduction

With the introduction of various environmental technologies, such as cell hooding, high draft ventilation and alumina dry scrubbing, the primary aluminium smelting industry has made great progress in reducing its environmental footprint. In contrary to many of the aspects, the release of spent potlinings is still work in progress. Some people claim that good solutions are available to re-use or have SPL processed, but others may disagree and still send SPL to a disposal site (where it does not belong).

Spent potlining (SPL) is the collective of lining materials after it has been removed from a cell after its useful life. Because of penetration by fluorides and the formation of cyanide complexes, the material is deemed to be a hazardous waste and must be managed that way. Rickman [1] presented a simplified diagram with the general composition of SPL a shown in Figure 1.

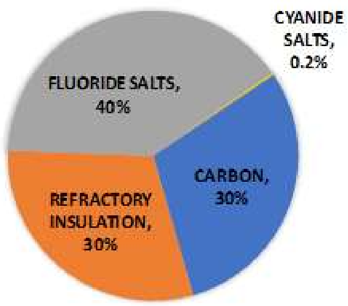

Figure 1. General composition of SPL (from Rickman [1]).

2. The Penetration and Transformation of Cell Lining Materials

2.1 Reactions within the Cathode Carbon Materials

When a cell is provided with a new lining, the lining materials are made from clean and virgin carbon materials. The cathode carbon materials typically have a porosity between 15 and 25 %, but it only becomes penetrated by bath materials after electrolysis is started. The penetration is initiated by metallic sodium followed by the electrolyte, as is presented by Sørlie and Øye [2]. Table 1 shows the reactions occurring within the cathode.

Table 1. Chemical reactions within the cathode carbon [2, 3].

EQN.	CHEMICAL REACTIONS	ΔG^o (kJ)
	The origin of Na(C), CO, NaCN, and Na_2CO_3:	
1	6 NaF + Al (l) = Na_3AlF_6 (l)) + **3 Na(C)**	+41.7
2	0.5 O_2 (g) + C (s) = **CO (g)**	-220.0
3	4.5 CO (g) + 3 Na(C) = **1.5 Na_2CO_3 (l)** + 3 C (s)	-209.1
4	1.5 N_2 (g) + 3 Na(C) + 3 C (s) = **3 NaCN (l)**	-164.7
	The reactions that change the cryolite ratio:	
5	0.75 Na_3AlF_6 (l) + 1.5 CO (g) + 3 Na(C) = **0.75 $NaAlO_2$ (s)** + 4.5 NaF (l) + 1.5 C (s)	-346.5
6	0.75 Na_3AlF_6 (l) + 1.5 Na_2CO_3 (1) + 1.5 C (s) = 3 CO (g) + **0.75 $NaAlO_2$ (s)** + 4.5 NaF (l)	-137.8
7	Na_3AlF_6 (l) + 0.5 N_2 (g) + 3 Na(C) = **AlN (s)** + 6 NaF (l)	-225.0
8	1.5 Na_3AlF_6 (l) + 1.5 NaCN (1) + 3 Na(C) = **1.5 AlN (s)** + 9 NaF (l) + 1.5 C (s)	-255.0
	The reactions that consume NaCN are Eqn. 8 and:	
9*	3 Al_2O_3 (s) + 1.5 NaCN (l) + 3 Na(C) = **4.5 $NaAlO_2$ (s)** + **1.5 AlN (s)** + 1.5 C (s)	-214.8
	Additional formation of $NaAlO_2$:	
10	3 AlN (s) + 6 CO (g) + 3Na(C) = **3 $NaAlO_2$ (s)** + 6C (s) + 15N_2 (g)	-711.0
11*	Al_2O_3 (s) + CO (g) + 2Na(C) = **2 $NaAlO_2$ (s)** + C (s)	-217.7
	Formation of Al_4C_3:	
12	Na_3AlF_6 (l) + 3Na(C) + 0.75C (s) = **0.25 Al_4C_3 (s)** + 6 NaF (l)	-74.3
13*	2 Al_2O_3 (s) + 0.75 C (s) + 3Na(C) = **3 $NaAlO_2$ (s)** + **0.25 Al_4C_3 (s)**	-47.5

*It is noted that in Equations 9, 11, 13 the alumina data is for α-Al_2O_3 as data for the actual similar compound β-Al_2O_3 ($Na_2O\cdot 11Al_2O_3$) is not available. In the equations with Na(C) data, data from Na (l) was used. This means that the actual ΔG^o is slightly more negative when Na(C) is on the right side of the equation and slightly more positive when Na(C) is present on the left side.

2.2 Salt Composition Within the Cathode

Cores from 16 industrial carbon cathodes were divided into 5mm slices and analyzed for its salt content [3]. Sodium metal was not analyzed but was earlier found to be up to 6%. Figure 2 presents the average composition for the cores as function of age. The figure shows that the cathode contains about equal amounts of Na_3AlF_6 and NaF, with a final concentration of about 30 wt%. Interesting is that the measured cryolite ratio is about 8 and this is much higher than in the electrolyte. Another observation is that the amount of oxides relative to AlN is less than the composition in air. Both effects are a result from the reaction with sodium (Table 1 / Equations 5 - 8).

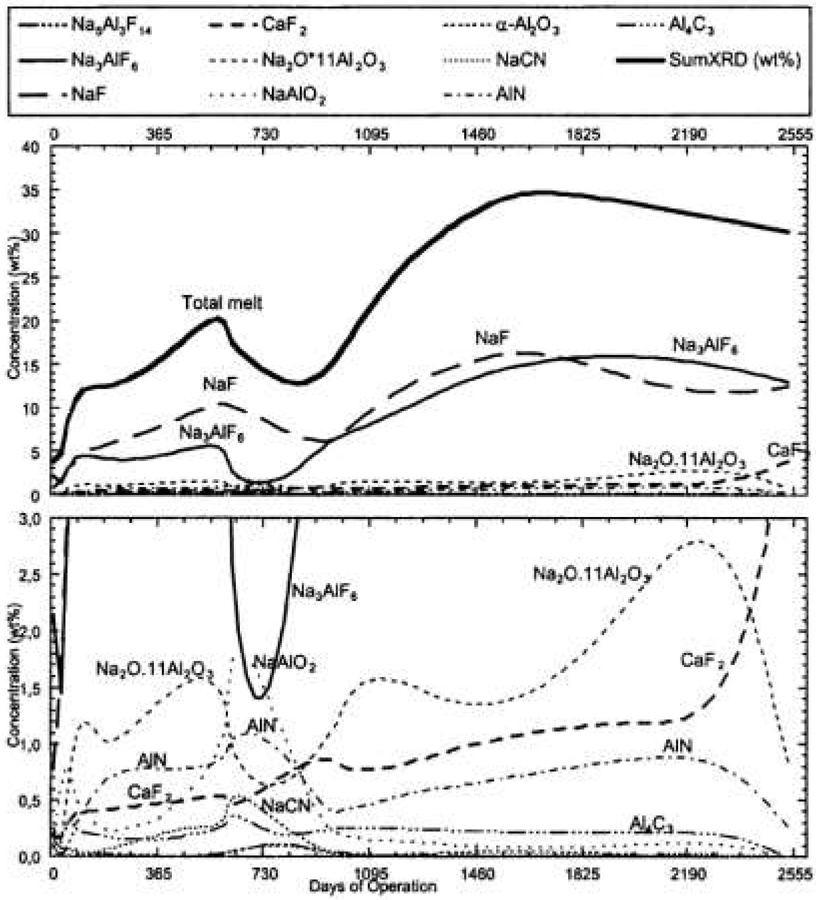

Figure 2. Evolution of the melt component phases (wt%) over time given as the average in the lining [3].

2.3 The Hazardous Properties of Spent Potlining

Spent potlining is classified as a hazardous material for three reasons:

- Its content of fluorides
- Its content of NaCN, and
- The reactions with water that lead to the formation of potentially explosive gases.

Spent potlining is generally generated from pots >1500 days and contains up to 15 wt% NaF and 15 wt% Na_3AlF_6 (See Figure 2). If SPL comes in contact with water, such as ground water, it leaches fluorides to create a contamination of water that could be a source of drinking water. The second factor that marks SPL as hazardous is its content of cyanide. The values vary but SPL may contain up to 0.2 wt% of cyanide salt. The formation mechanism of cyanide is directly linked to the penetration of sodium. The cathode is not vacuum tight, which makes it possible for air to penetrate the lining. The nitrogen of the air reacts with sodium to form NaCN (Table 1 / Equation 4) that becomes embedded in the cathode material. The figure shows that NaCN content is highest in young cells but partially back reacts in older cells with cryolite or alumina to form AlN (Table 1 / Equations 8 and 9).

SPL contains some salts that by themselves are not hazardous but when in contact with water form gases that pose a danger. In several standards, such as the NFPA, SPL is classified as a water reactive material. More about this later.

The reactive species are Na, Al, AlN and Al_4C_3. Augood [4] investigated the gas evolution potential based on the following reactions and reaction products:

$$Al_4C_3 + 6\ H_2O = 3\ CH_4 + 2\ Al_2O_3 \quad (14)$$
$$2\ Al + 3\ H_2O = 3\ H_2 + Al_2O_3 \quad (15)$$
$$2\ Al + 2\ NaOH + 2\ H_2O = 3\ H_2 + 2\ NaAlO_2 \quad (16)$$
$$2\ AlN + 3\ H_2O = NH_3 + Al(OH)_3 \quad (17)$$
$$2\ Na + 2\ H_2O = H_2 + 2\ NaOH \quad (18)$$

Bath also contains phosphorus and some of this may penetrate the lining materials as well. In those cases, researchers will also find phosphine (PH_3) in the gases that is released from SPL. This is a toxic gas; however, the concentrations are typically 100 to 200 times lower than ammonia or methane.

Augood has been one of the few researchers that were able to report on the gas evolution rates. His research showed a maximum rate of 18 m^3 per tonne of SPL with 36 vol% methane, 14 vol% hydrogen and 50 vol% ammonia. This is an average composition that is a function of temperature and concentration of NaOH. Water that gets into contact with SPL will react quickly with Na to form NaOH. Hydro Aluminium [5] conducted experiments that show results that are in reasonable agreement with this. Their results show gas evolution rates that range from 6.5 to 8.7 m^3 per tonne. A value found by Alcoa is 5.7 m^3 per tonne of SPL.

2.4 Heat Release During the Evolution of Gases

When keeping SPL in storage there is the potential for fires that must be accounted for with measures. The National Fire Protection Association (NFPA) has available standard NFPA 400 that governs the classification of a material like SPL. SPL is a water reactive material that falls under section A.3.3.60.11. and its classification will set certain technical requirements to prevent or fight fires should one occur. The classification is driven by the energy that is released when the gases evolve from SPL. If enough energy is released, then the gases can be ignited by this. The reactions have a negative enthalpy which means that heat is released.

Reactions:					**ΔH^0_f (kJ/mol)**
$Al_4C_3 + 6H_2O \rightarrow 3CH_4 + 2Al_2O_3$					- 1720
$2AlN + 3H_2O \rightarrow 2NH_3 + Al_2O_3$					- 269
$2Al + 3H_2O \rightarrow 3H_2 + Al_2O_3$					- 812
For 1 kg of SPL			**Xi ΔH^0_f**		**Heat**
	mol	Volume %	kJ	cal	cal/g
CH_4	0.198	36	- 113.5	- 27 133	- 27.1
NH_3	0.271	50	- 72.8	- 17 401	- 17.4
H_2	0.078	14	- 42.2	- 10 075	- 10.1
Total	0.840	100	- 228.5	- 54 609	- 54.6

Figure 3. Calculations to determine the heat released from the chemical reactions.

The result, as shown in Figure 3, is that approximately 55 cal/gram (230 kJ/kg) of heat is released. In NFPA 400 this makes the material fall in the range 30 to 100 cal/gram. SPL as per this example is therefore a Class 1 water reactive material.

2.5 Corrosive Properties

If water comes into contain with SPL, then NaOH will immediately dissolve in the water. The pH of the water will become very high (> 10), which means the water is corrosive to many materials. The same is true when SPL comes in contact with the human skin. The caustic will react with the moisture in the skin and can cause burns or blisters.

3. Generation of SPL

There comes a moment that a cell is taken off line to replace the lining with a new one. For low amperage cells this can be in range of 2500 days from startup and for high amperage cells this can be around 2100 days since the startup. After the power has been disconnected the cell can cool down. Once the cell is cooled down the delining work can start. In some cases, delining and relining takes place inside the potroom; however, modern potlines have a dedicated area where pots are delined followed by relining.

The average delining capacity is nominally 3 to 5 cells per week. In large smelters such as EGA Al Taweelah (EMAL), for example, the required rate is much higher and exceeds 7 cells per week. New smelters will often only have their delining facility added about 4 years into operations. It saves capex for the main project and it is not really needed yet since the life of pots is more than 4 years. But at some point a facility is required. It is important to do a good analysis on the peak production of cells coming off line as this determines the design rate for delining. The difficulty is that this rate normally only occurs in the first cycle of cells. After that, the curve of cells coming off line flattens and the rate is lower.

A modern delining facility will have several containers lined up that are filled during delining. By doing so it enables the smelter to generate two separates cuts of SPL material. One carbon rich cut and one refractory rich cut. This enhances the ability to have the material recycled. A future challenge will be recovery of cathode collector bars that have copper inserts. These are expensive, and efforts will be required to ensure that all copper is recovered. This may reduce the rate of delining.

Older cell technologies and technologies in China typically produce 20 to 30 kg SPL per tonne aluminium produced whereas modern high amperage cell technologies typically produce 16 to 20 kg SPL per tonne. The split between first cut and second cut depends on the design of the lining but a good number is a split of 55:45 in weight.

4. Storage of SPL

There are cases where the containers with SPL can be taken to the disposal right away. Or that intermodal containers are used, such as from PIC360, whereby those containers can be used as temporary storage on site prior to shipping them off to the end user. However, in most cases a dedicated SPL storage facility is used to create a buffer between delining operation and end-user. The size of the building depends on the inventory that is kept. An indicative range is 4 to 10 tonne SPL per m^2 of floor area. Some examples of storage buildings are presented in Table 2.

Table 2. Examples of SPL storage buildings in aluminium smelters.

Location	Storage capacity	Floor area	Ventilation type
Portland Aluminium	25 000 tonnes	90 m x 32 m	Mechanical
Sohar Aluminium	32 400 tonnes	145 m x 35 m	Natural
EGA Al Taweelah	50 000 tonnes	175 m x 45 m	Mechanical + Natural

When a smelter decides to install a storage facility, it has the choice to apply a minimal set of requirements to the building, or to be a leader and take measures that are good for the environment and the workers. A good example is the new storage building at EGA's Al Taweelah smelter where EGA consciously incorporated both natural and mechanical ventilation features to have the highest level of ventilation possible.

Floor design

The building must prevent direct contact with any water and if any water enters the building, it must be diverted and collected. The walls of the building are integrated with the floor to make it a tub. This way it is fully contained and nothing leaks from the floors. There is a slope to ensure any free water runs off to a collection system.

Wall design

The walls are sealed and integrated with the floor. If it is a free-standing wall, then it stands up to 4 or 5 meters high. The roof can overhang with overlapping vertical siding so that air can flow through, but that rain is kept out. If mechanical ventilation is applied, then the axial fans to push air inside the building are positioned in the walls.

Roof design

The roof provides a rain free environment but will have ventilation channels in the center. The air must be able to flow freely and if only natural ventilation is applied then a draft must be created to induce the airflow.

Fire protection and explosion proofing

A fire detection system is included, and only dry methods of firefighting are allowed. This means a sprinkler system is not used, which requires some explanations to local fire authorities. Electrical devices should be dust and explosion proof.

HSE measures

PPE must include wearing facemasks. Monitoring of gases such as ammonia is required in some cases. Some companies have the requirement that all equipment leaving the building must be cleaned from dust prior to departing from the area. This maximizes the containment of SPL dust.

Ventilation design

The ventilation of the building should be designed so that enough air flow exists or that there are enough air changes that LEL levels of methane and hydrogen gases are kept at maximum 20 to 25% of their allowed levels.

5. Transportation of SPL

In this section is described some examples of transporting SPL. Always check with local authorities first because the requirements are not uniformly applied. What is allowed in one country, may not be permitted in another.

In most operations containers are the first means of moving SPL. From delining to storage building requires only standard containers and they are only moved when it is dry and does not rain. For regional transport more requirements will apply since now a hazardous waste is leaving the facility. A trucking company must be used that is licensed to haul hazardous waste and has trained drivers. Containers with raw SPL must be water tight using at least a tarpaulin cover (Ref. VC1). They also must be able to breath (=ventilate) so that no accumulation can occur (Ref. AP2). Containers with ground SPL should be of isotainer type that are fully sealed. In both cases a protocol must be in place that guides the trucks when and when not to drive but also what to do if there is an accident and some SPL is released from a container. There are also MSDS sheets available online from Alcoa or from Rio Tinto as examples.

There are examples where SPL is loaded in 1 tonne supersacks and then placed into containers for transport. One must be careful with supersacks as small tears can mean a release of SPL dust.

Bulk transport inside ships is not recommended or probably not even allowed anymore. The most serious accident with SPL that ever happened was a vessel carrying SPL that exploded in Port Alfred, Quebec, Canada on 19 March 1990. Its forward hold exploded after water had entered this hold. Because it was sealed, explosive gases had accumulated. A large explosion resulted killing two people and causing $30M in damage.

For long hauls hazardous waste type containers are used. These are limited in supply and require some planning ahead for international shipments. One good example of a container is the intermodal container from PIC360. This is purposely built and used widely for international shipping of SPL. In Europe the UNECE recently made changes to the requirements for containers to transport UN3170 waste [6]. In the new rules only BK2 type containers can be used.

Generally, SPL is transported in course or crushed form. It does not happen very often that SPL is shipped in a finely ground form. One example where this does take place is Boyne Smelters where finely ground SPL is prepared and dried in the old Comtor plant. It is filled into isotainers and taken to a cement plant for direct injection.

SPL listed as a hazardous waste under the Basel Convention that controls transboundary movements of hazardous waste and their disposal. This means an international shipment across borders will require permits and documentation that follow the regulations of the convention. It also requires that countries which the material is passing through, be notified of this. For a company to establish the documentation for the first time, this requires a considerable effort and the timeline is 6 to 10 months to get this in place. After that it will be a lesser effort. This is the recent experience of EGA that shipped 4619 tonnes of SPL to Befesa in Spain [7].

In the US, SPL is classified by the EPA in the code of federal regulations as K-088 (Ref. 40 CFR part 268 and 271). The EU has listed SPL in the EU Waste Catalogue under No. 161101 “Carbon-based linings and refractories from metallurgical processes containing dangerous substances” and No. 161103 “Other linings and refractories from metallurgical processes containing dangerous substances”. Under the Basel Convention SPL is categorized as waste material A4050 “Waste that contains inorganic cyanide”. The number assigned by the United Nations Committee of Experts on the Transport of Dangerous Goods is UN3170 and the sub-classification is class 4.3, which is used to mark the containers for transport by truck. Note that this is a current list and may be subject to changes in the future.

6. SPL Solutions

Today, there are several solutions available to smelters when a management plan is developed. These are described below. There are also some solutions that are on the peripheral and perhaps of interest in the future or in special cases. These are mentioned but not discussed in detail.

6.1 Options Analysis

A smelter first needs to identify what the options are for their SPL. To identify the best option (or two), one good method to use is to develop a matrix in which one can evaluate the various options. Such matrix can look like the one presented in Table 3:

Table 3. Matrix for evaluation of SPL options.

Evaluated aspect	Solution A	Solution B	Solution C
Cost for preparing SPL prior to shipment	1 to 5	1 to 5	1 to 5
Cost for processing by 3rd party	1 to 5	1 to 5	1 to 5
Transportation cost and other fees	1 to 5	1 to 5	1 to 5
Maturity of the solution	1 to 5	1 to 5	1 to 5
Both cuts or only 1 cut	1 to 5	1 to 5	1 to 5
Contract type	1 to 5	1 to 5	1 to 5
Environment footprint	1 to 5	1 to 5	1 to 5
Permitting effort	1 to 5	1 to 5	1 to 5
Impact in liability	1 to 5	1 to 5	1 to 5
Contribution to the local economy	1 to 5	1 to 5	1 to 5
SCORE	Total for A	Total for B	Total for C

Obviously, more aspects can be evaluated depending the needs of the team involved. A team should really develop this because then the scores will be balanced, and the outcome is accepted by all and can be carried forward to a level of decision making. This matrix can also be used to evaluate if the current option is still the best.

An added tool is to prepare a cash flow analysis. If an investment is required and costs are incurred over time, then different projects can be compared using a cash flow analysis to identify the net present values.

6.2 Storage of SPL

Although not considered a sustainable solution, shipment of SPL to a landfill or long-term storage is still a commonly used solution. In fact, more than 50 % of the produced SPL is landfilled without any special treatment. The main reason is that it provides certain flexibility and that the cost per tonne of SPL is often low.

There are smelters that still have an on-site landfill but, in most cases, it is a third party like Waste Management in the US that operates several Subtitle C facilities to dispose of hazardous wastes. Another example is found in Norway where NOAH operates a disposal site on Langøya Island. This is an old quarry where SPL is mixed with waste gypsum to stabilize the material. The facility that manages the landfill must have proper technical features in place to collect the runoff water and treat this. It will contain cyanide and fluoride among other constituents that co-exist in the disposal.

Legislation varies between countries, but a usual minimum requirement today is storage in a building or a covered pit with a non-permeable base. To prevent fluoride contamination of drinking water from an earlier non-covered SPL site, it was required to drill under the landfill and pump up the run-offs for treatment.

Included in this section is also the practice to neutralize SPL in a basin that overflows with seawater when the tide is high. The seawater neutralizes the SPL over time and fluorides are not an issue for seawater as it holds plenty of calcium and magnesium. The residue is then permanently landfilled after it has been removed from the basin. This practice is no longer used in Norway but still used in Iceland by Nordural and ISAL. It must be noted that Nordural includes layering of crushed limestone to enhance the neutralization process.

6.3 Alcoa Gum Springs

In Gum Springs, Arkansas, Alcoa operates the largest SPL facility in the world rated at 109 000 tpy. This plant is based on the Reynolds process (Figure 4) and has been operational for over 25 years. Many smelters, including smelters not owned by Alcoa, ship their SPL to the plant where it is received and inspected. Metals are removed. The process is based on heat treatment in a rotary kiln. The SPL is mixed with limestone and sand and fed to the kiln. The product is treated for 90 minutes under temperatures in range of 550 - 800 °C and then discharged. The product was originally declared non-hazardous, but the delisting was withdrawn. The cooled material is taken today the on-site hazardous landfill that has the means to collect run off water and treat it.

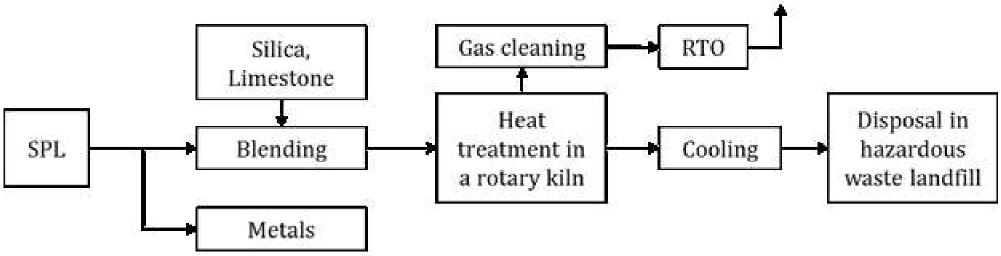

Figure 4. Simplified process diagram of the Reynolds process.

Alcoa is trying to diversify the site. Over the past years some of the SPL has been diverted to licensed cement plants. Only a very few cement plants are allowed to take hazardous waste as feed stock and this limits the opportunities in the US.

6.4 Rio Tinto UTB SPL Plant (LCLL)

In Jonquiere (Quebec, Canada), Rio Tinto operates the UTB plant for processing of SPL. It is developed to process SPL from old storages and fresh SPL from operating smelters. It can also process SPL cuts individually or mixed SPL. For its complexity it is rather flexible and by operating in campaigns specific byproduct qualities can be produced that are aligned with the end users. Another aspect is that the plant can also process other wastes from the smelter such as carbon fines and shot blast material. It currently operates at its nameplate capacity of 80 000 tpy and has already processed half of the 600 000 tonnes that were in storage at the start of the project.

This plant is based on the so-called low-caustic leaching and liming process also referred to as the LCLL process (Figure 5).

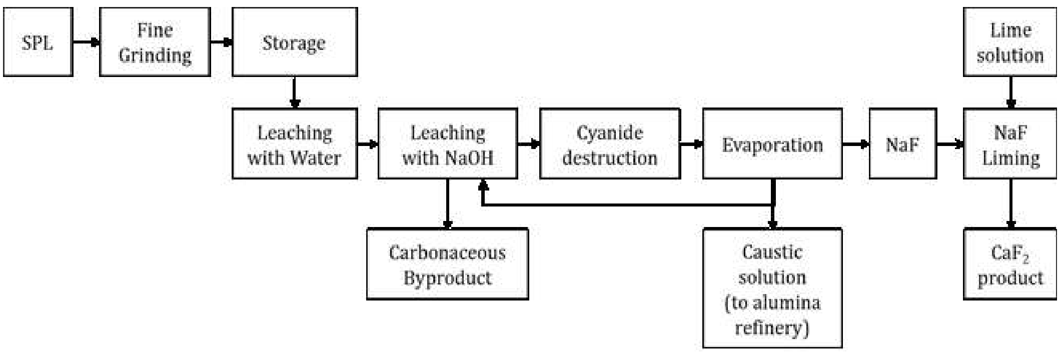

Figure 5. Simplified process diagram of the LCLL process [8].

According to Rio Tinto the state and quality of the received SPL is not leading to any problems when the material is added to the process. Rio Tinto manages the input in order to obtain specific byproduct qualities. The inert byproducts are used in cement and steel industries. The calcium fluoride product is still being landfilled for the time being; however, research shows that if the material is dried that is can be mixed with the feed of the acid kiln to make aluminium fluoride. It has to be very dry in order not to have a negative impact on the kiln economics at the AlF_3 plant. If further treatment is applied (i.e. calcination) then the materials can be directly used in the acid kiln but also in steel applications. The expectation is that be 2020 a process solution is implemented and that all CaF_2 is reused.

Rio Tinto is working on an important process improvement that saves about 40% of the steam requirements [8]. By only evaporating what is required, a part of the sodium fluoride can be bypassed to the liming process. By doing so the throughput in the evaporator is reduced leading to the savings in steam consumption. These changes are referred to as LCLL-2.

6.5 Co-processing of SPL in Cement Plants

Perhaps one of the most sustainable solutions is co-processing of SPL in the production of clinker followed by cement (Figure 6). The elements that are present in SPL are almost all a match with the clinker process. The carbon is used as fuel, the refractory part is making up the raw materials and the fluoride enhances the mineralization. It allows for a 100 °C lower kiln temperature which results in a higher alite content. Because of this the clinker factor is improved leading to good operational improvements against little investments. In the kiln the process is operated in excess of 1300 °C and under those conditions all cyanides are completely destructed.

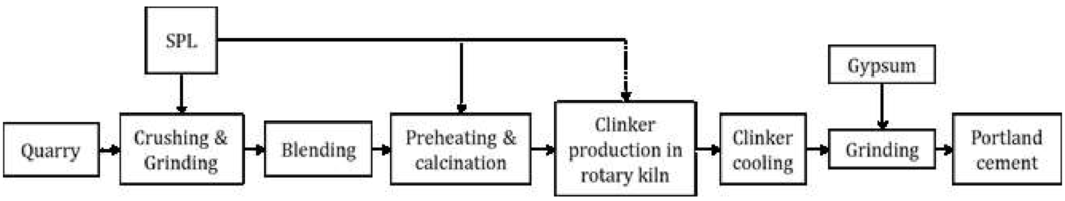

Figure 6. Simplified process diagram of production of clinker and Portland cement.

There are challenges with the addition of SPL to the clinker process. SPL contains a large amount of sodium (Na). Sodium is tightly controlled in the process because it has detrimental effects in concrete if the concentration is too high. Cement plants that operate with high alkalinity in the raw materials will have a hard time adding SPL. Plants with low alkalinity can add SPL up to 0.25 wt%. What is also problematic is that the sodium content of SPL varies like most constituents. This also limits the amount that is added. In a similar manner is also the fluoride addition limited. Too much will also have a negative impact, so it is tightly controlled. Furthermore, in the preparation upstream care is taken to remove metallic aluminium from the SPL. If the cement plant uses roller type crushers to produce the raw meal, then the SPL must be thoroughly cleaned from metallic aluminium because it otherwise gets stuck inside the rolls. A ball mill circuit does not have such problem and can do with a normal level of metal removal.

Because there are many cement plants in the world and the capacity of a single plant is large, it holds great potential to co-process a very large volume of SPL produced in smelters. It will be in most cases a regional solution because adding serious costs for transportation won't make sense. For this reason, other options will be needed in regions where the direct addition of SPL is not feasible.

Full scale co-processing of SPL started in France around 1999 [9]. Early adopters were found in Brazil, South Africa and the US. Recently activities are found in Australia (Boyne Smelters) and the Middle East where Sohar Aluminium, EGA and Qatalum all send SPL to cement plants. India is at the early stages of developing several routes to cement plants. Some large-scale trials have been approved (or started). It is worth noting that some of the cement companies have alternative fuel and raw materials (AFR) departments that have experience introducing SPL in their plants. An AFR department can play an imported role in establishing new relationships with cement plants.

6.6 The Regain Process

Regain Materials (Melbourne, Australia) created a process that is designed to overcome some of the challenges that exist with sending SPL to a cement plant. Regain mixes and homogenizes the feed stock and runs this through a mild thermal treatment to destroy the cyanide. It also quenches the heat-treated granules in water to deliberately drive off any of the toxic and explosive gases. These are then burnt in the kiln used for the heat treatment. The granules are dried and bagged for distribution. Regain runs the plants in campaigns so that is can target specific product qualities. They standardized their products which are marketed under brands names '*Hi-Cal*' kiln fuel and '*Re-Al*' high alumina additive. A Regain plant does not create waste water and recycles any solid wastes in the process (Figure 7).

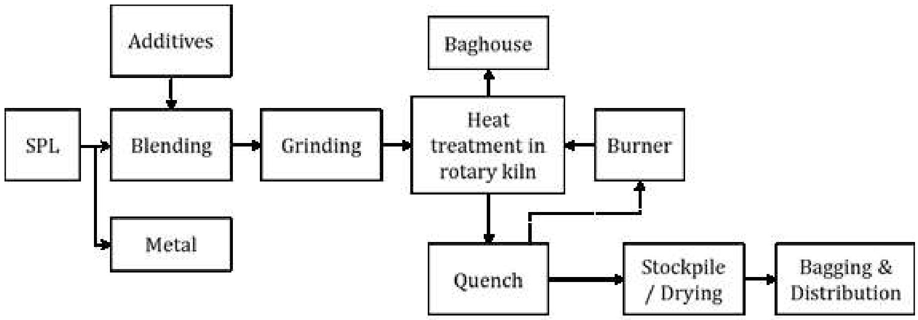

Figure 7. Simplified process diagram of the Regain process.

Regain built a total of three plants: one in Pt Henry, one in Kurri Kurri and one in Tomago. All plants combined have processed over 200 000 tons of SPL [10]. A plant can process first cut, second cut and mixed SPL. It does also offer the possibility to blend in other waste materials. Plants are relatively small and can be placed onsite a smelter. Today, this technology is the only merchant technology that can be built as a standalone unit in or near a smelter. Regain has established that its products are no longer considered hazardous. The products can therefore be exported through normal channels. This means it overcomes the difficulty of shipping SPL products internationally. Another important feature of the technology is that Regain has established a market for the products comprising of several cement and brick manufacturers internationally. Often this aspect is overlooked as it takes a lot of effort to establish off take contracts for SPL materials.

6.7 The Befesa Process

Befesa (Spain) first focused on the treatment of large volumes of spent salt slags that are produced by the secondary aluminium industry [11]. These salt slags are a hazardous waste but treated and recycled back to the secondary producers. The technical staff of Befesa recognized that the salt slag process could be used to treat SPL as well (Figure 8). In fact, they found that by blending three parts of salt slags and one part of SPL both material can be processed together with only modest adjustments. An interesting aspect is that Befesa can choose to include SPL or not. It is not reliant on SPL.

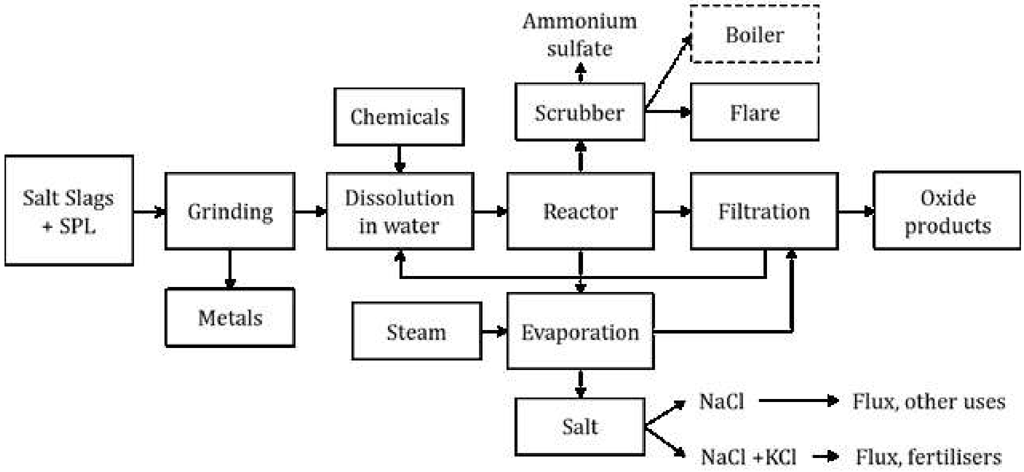

Figure 8. Simplified process diagram of the Befesa process [11].

By mixing the SPL with salt slags it passes through the process and becomes detoxified. All cyanides are destructed with chemicals. The solids are filtered from the process and dried so that they can be used in other industries such as cement, ceramics, bricks, mineral wool, civil works, high alumina refractories, and steel. No other wastes are formed.

Befesa operates five facilities: three in Germany, one in the UK and one in Spain and all of them can co-process SPL. The SPL process is registered as Best Available Technology (BAT) and has all ISO certifications. Befesa are also very experienced with handling international shipments. Over the years Befesa received SPL from various smelters worldwide including from the UAE, Australia and New Zealand.

6.8 The Use of First Cut SPL in DRI-EAF Steelmaking Furnaces

Steelmaking plants have traditionally been one of the users of SPL or SPL related products. However, recently a good solution has gained popularity after successful implementation by Qatar Steel. This refers to a steelmaking plant that uses electric steelmaking furnaces and where iron ore pellets are pre-reduced in so-called DRI pellets. These furnaces apply a foaming slag practice to maximize the efficiency for the input of electrical energy into the process (Figure 9). Coarse carbon is used which can be replaced with first cut SPL. The benefit for the steel plant is a cost saving in raw materials.

The carbon is consumed in the interface between liquid steel and slag. At temperatures well above 1000 °C all cyanides are destroyed, and non-carbon elements become part of the slag. The slag is mainly made up of lime (CaO) and almost all fluoride is caught as CaF_2. The stack gases see some HF concentrations, but these are below limits.

To feed first cut SPL to the EAF furnace it only has to be crushed to 50 to 80 mm in size. This makes preparation and its use easy, but it does mean a fine fraction is left behind. In Sohar (Oman) Jindal Steel has started taking first cut SPL in 2017. They receive this from Sohar Aluminium who crushes the SPL first to make it ready-to-go for Jindal. In Qatar, Qatar Steel receives first cut as it is received from Qatalum.

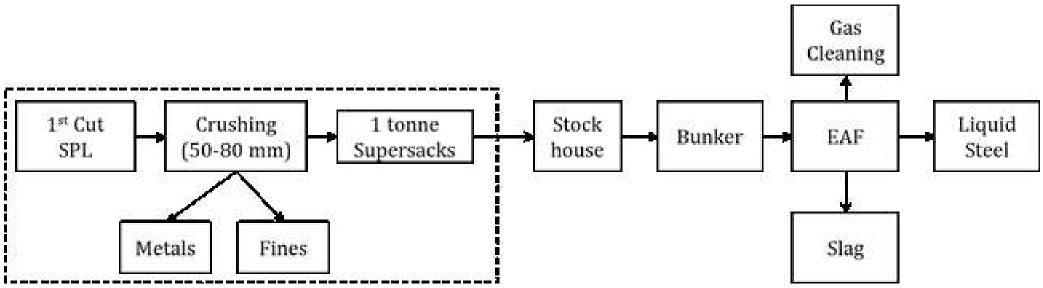

Figure 9. Simplified process diagram of using first cut SPL in DRI-EAF steelmaking.

6.9 SPL Processing by Weston Aluminium

Weston Aluminium (Kurri Kurri, Australia) started as a dross recycling operation. It uses rotary furnaces to recover aluminium in a salt-free process developed originally in Japan. Driven by excess production capacity, it started looking at processing SPL several years ago. It first tested second cut SPL with good success. Today, they process both first and second cut SPL from Hydro Aluminium's Kurri Kurri and from Portland Aluminium.

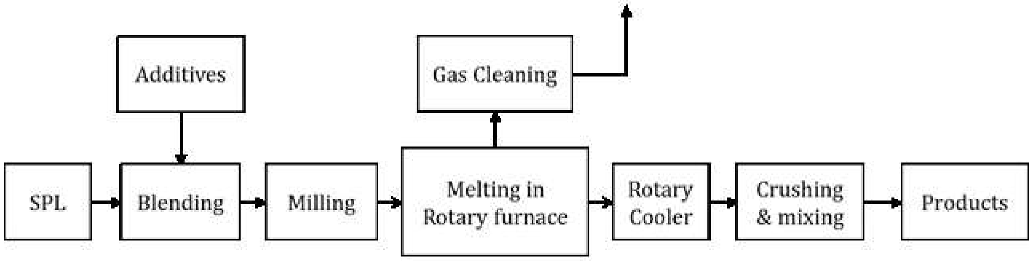

Figure 10. Simplified diagram of the SPL process developed and used by Weston Aluminium.

SPL is processed in batches [12]. It is milled and mixed with additives such as glass cullet and iron oxides. The material is fed to the rotary furnace where it is heated at moderate temperatures (< 900 °C) to destruct cyanides but to avoid releasing sodium and fluoride. The off gases are cleaned using a lime scrubber followed by a baghouse. After a batch is completed the material is cooled in a rotary cooler. The product is crushed and mixed with further additives if required. The material is shipped to end-users in Asia. The process is designed keeping in mind the end-users, which mainly are brick manufacturers in Asia. The brand name of the product is '*Neverflux*' and it enables brick manufacturers to increase production with little effort.

Weston Aluminium is fully licensed to process up to 40 000 tonnes per annum of a combination of dross and SPL. This means that they can nominally process up to about 20-25 thousand tonnes per year of SPL. The products are targeted mainly for use in road construction.

6.10 Other SPL Technologies and Initiatives

Above are described the main processes that are used to treat SPL commercially and on full-scale basis. However, there are some other technologies and initiatives worth mentioning that could become more prominent in the future.

6.10.1 First Cut SPL Used in Production of Stone Wool

Rockwool is a major stone wool producer that operates cupolas to melt basalt into a glass material that is then transformed into insulation materials or other products. To reduce costs, they accept certain waste materials that are mixed in with their feedstock. The cupolas use carbon materials in the process and this material can partly be replaced by first cut SPL. In the process 2 to 3 tonnes of first cut SPL replaces 1.3 to 2 tonnes of coke. According to Rockwool this can save 20 to 25 % in energy requirements.

Until recently Rockwool processed all SPL from Hydro Aluminium and some from Trimet. But Hydro did not renew the contract after Rockwool had difficulties in their process. Because of this uncertainty we list it under the alternatives for now. However, the volume of SPL this industry could potentially process is very large, so it is hoped that this practice can continue also outside of Germany.

6.10.2 The Oriens process

The roots of Oriens are with NovaPB, a company from Montreal (Canada) that no longer exists, but where the original Calsifrit process was invented. Oriens continued the development but adapted the process for use in rotary furnaces, the same types used in recycling dross. According to Oriens this makes the process much more robust. It is very similar to the approach of Weston Aluminium with the difference that it targets to make a byproduct that is '*Calsifrit'*, which can be used directly in Portland cement.

Oriens operated a demo plant in Bécancour, Quebec, with a full-size furnace processing SPL obtained from smelters in the region. It is now looking overseas for a first commercial application. The technology can be packaged as a merchant technology and built onsite or near a smelter.

6.10.3 Plasma Vitrification Technologies

Elkem has developed smelting process where crushed and screened SPL, quartz and iron ore are charged to an electric smelting furnace. The products are pig iron and a slag. The molten slag can be reacted with steam to produce AlF_3, which is a necessary raw material for the aluminium electrolysis process. The process was tried in a full-size smelting furnace but has now been stopped.

On the other hand, UK-based Tetronics offers a plasma process based on their proprietary plasma technology. For SPL they have formed a partnership with Harsco, a well-known provider in metals and resource recovery services. It is understood that this partnership sold one plasma vitrification plant to Talum in Slovenia.

6.10.4 The Engitec SPL Process

The Italian firm Engitec is known for its spent salt recycling process that they started with in 1977. Recently it has decided to focus on processing SPL in a new process. In the process SPL is leached with a caustic soda solution followed by an electrochemical treatment for the regeneration of the leaching chemical (NaOH) [13]. The solids are filtered and made ready for third party uses. The electrochemical cell produces a slurry of primarily cryolite and aluminium hydroxide that is separated using filtration. If the cake is calcined, then the resulting mix is cryolite and alumina.

Engitec is building a modular pilot plant for 360 kg SPL/day and is seeking partners to develop the process to a next level. Well beyond that, Engitec believes that this new process can be integrated with their latest version of the STE process for salt slag recycling.

6.10.5 Initiatives by Aluminium Companies Directly

It is worth mentioning that there are aluminium producers that develop their own initiatives.

- UC Rusal reported to be working on a new hydrometallurgical process that uses a water/NaOH leaching step to extract fluorides from SPL. They also implemented a practice to finely crush refractory material and re-use this as insulator in new the lining of new cells [14].
- In India Hindalco is reportedly working on a cryolite recovery process.
- Various small initiatives with recycling or resource recovery companies.

6.10.6 Developments in China

Going by the list of recent patents, the Chinese institutes are actively looking for new processes to recycle SPL. Most patents filed on SPL in the last 5 years are Chinese. In addition, Chalco had built two SPL processing plants that operated for some time. Furthermore, the development of a new vacuum distillation process at 1200 °C for spent carbon cathode blocks is promising [15]. Na_3AlF_6, NaF and sodium metal are effectively separated. The carbon content after distillation is above 91%, and the impurities are mainly CaF_2 and Al_2O_3. A 50 tonnes furnace is presently in operation [16]. However, it is not transparent what exactly happens with SPL in China and with an 'environmental penalty' of only 1000 RMB per tonne (US$ 145/t) there is no good incentive to use dedicated processes to recycle or process SPL.

7. Conclusions

With this paper insights are provided on how the lining of cells changes and why it is deemed hazardous after it is removed from a cell and become SPL. Because of its hazardous classification it must be stored, handled and transported with care and specific measures. Some industry examples and experiences are described as well as some specific requirements set under standards like by the NFPA. This all provides good understanding of how to manage SPL in a smelter.

It has to be concluded that today still a very large portion of SPL is sent to landfills. While everyone agrees that this is not a sustainable solution, the cost is often still acceptable and the flexibility it offers is another compelling reason to use a landfill. But slowly the landscape is changing. There are now more than ever technologies and processes available that can reuse, co-process or otherwise make SPL non-hazardous. There are processes dedicated to transformation of SPL and then there are process in which SPL is regarded a raw material replacement. In some cases, the objectives are combined when SPL is detoxified and made a raw material for an industry like cement production.

Table 4 shows that a smelter has options to evaluate for managing its SPL. Depending on their location an analysis will show what the best option is.

Table 4. Summary table of mature SPL solutions.

Process	Market	Product use
Landfill	Regional	Storage
Alcoa Gum Springs	International	Landfill / Cement
Rio Tinto UTB	Regional	Steel / Cement / Landfill
Cement plants	Regional	Portland cement
Regain Materials	Onsite / Regional	Cement / Brick
Befesa	International	Cement / Various others
EAF Steel production	Regional	Steel
Weston Aluminium	Regional including New Zealand	Brick

There are solutions on the peripheral that can be considered in the near future. There are shown in Table 5. We mark that the Rockwool option could be reactivated and has large potential once everything is back on track. In the meantime, companies like Oriens and Engitec will continue their developments to seek a first commercial plant and pilot plant, respectively.

Table 5. Summary of promising processes that may have an impact in the short-term.

Process	Market	Product use
Rockwool	Regional	Stone wool
Oriens	Onsite / Regional	Portland cement
Tetronics	Onsite / Regional	Road construction
Engitec	Onsite	Cryolite & Alumina

The focus is mainly on SPL solutions available in the rest of the world. China is an isolated case where many research activities take place and some newer technologies are being developed. The vacuum distillation approach being one of them. However, it is very difficult to say in what direction China goes or if any of these technologies could be used in the rest of the world. That will be left for a future publication.

In close, a reasonable number of good solutions are available for smelters to have their SPL processed in a responsible way. There is no silver bullet and each will have pros and cons to consider. And although this paper does not elaborate on costs, the reality is that the options will remain a cost issue for some time to come.

8. References

1. W.S. Rickman, Circulating Bed Combustion of Spent Potlining, *Light Metals* 1988, 735-743.
2. Morten Sørlie and Harald A. Øye, *Cathodes in Aluminium Electrolysis*, 3rd Edition 2010, Aluminium-Verlag, Dusseldorf.
3. L.P. Lossius and H. A. Øye, Melt penetration and chemical reactions in cathodes during aluminium electrolysis, *II. Industrial Cathodes. Met. Mat. Trans.* 31 B (2000), 1213-1224
4. Derek R. Augood, Some handling considerations for spent potlining, *Light Metals* 1986, 979-992.
5. A. Dyrøy, SPL - Straight forward or still a challenge?, *Seminar on Research and Advances in Smelting Technologies in GCC*, Qatar, May 26 - 28, 2015.
6. UNECE memorandum ref. ST/SG/AC.10/C3/2014/10.
7. M. Al Jawi, Spent pot lining recycling Emirates Global Aluminium, *IAI SPL Workshop*, London (2018).
8. S. Poirier, Recent update on the LCLL process, *IAI SPL Workshop*, London (2018).

9. P. B. Personnet, Treatment and reuse of spent pot lining – An industrial application in a cement kiln, *Light Metals* 1999, 269-276.
10. B. Cooper, Overview of Regain SPL solution, *IAI SPL Workshop*, London (2018).
11. C. Ruiz de Veye, Full recycling process for aluminium wastes, salt slags and SPL treatment and recovery, *IAI SPL Workshop*, London (2018).
12. Personal communication between the authors and Weston Aluminium (2018).
13. Personal communication between the authors and Engitec (2018).
14. Victor Mann et al., SPL recycling and re-processing, *Light Metals* 2017, 571-578.
15. Wang Yaowu, Peng Jianping and Di Yuezhong, Separation and recycling of spent carbon cathode blocks in the aluminum industry by the vacuum distillation process, JOM, Vol. 70, No. 9, 2018, 1877-1882.
16. H. A. Øye, Private Information.