

Discussion of Industrial Spent Pot Lining Treatment

Harald Arnljot Øye

Professor

Norwegian University of Science and Technology, Trondheim, Norway

Corresponding author: oye@material.ntnu.no

Abstract

Spent pot lining (SPL) from stopped aluminium electrolysis cells is an environmental problem. It consists of about 30 % carbon, 30 % refractory and isolation materials, 40 % fluoride salts and 0.2 % cyanide salts. Treatment of SPL is by hydrometallurgical or pyrometallurgical processes or pretreatment and addition to steel, cement or rock wool production. Established processes and processes under development will be discussed.

Keywords: Aluminium electrolysis, spent pot lining, detoxification, hydrometallurgy, pyrometallurgy.

1. Introduction

The aluminium industry has solved the problem with gaseous pollution by dry scrubbing using the alumina that later is added to the cell. The fluoride off gases may be as low as 0.2 kg F/t Al. Spent pot lining (SPL) which is dug out of stopped aluminium cells is still a problem. The composition is given in Fig. 1. Both the carbon and the refractory part are heavily impregnated with fluorides.

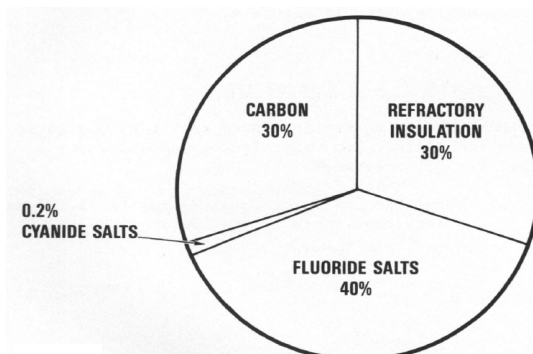


Figure 1. Average composition of spent pot lining (Rickman [1]).

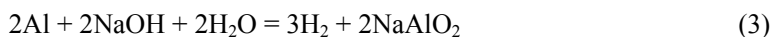
It is generated 18 – 35 kg SPL/t Al [2]; this translates to 1 to 2 Mt/year. Earlier it was thought that SPL could be recycled with a gain. Today the cost of detoxifying and recycling may easily amount to 1000 US\$/t. A large amount is only stockpiled. SPL is classified as hazardous waste as it contains fluorides, NaCN, Na, Al_4C_3 and AlN and is poisonous and potentially explosive. The SPL consists of a carbon part (First cut) and a refractory part (Second cut).

2. Watering Reaction

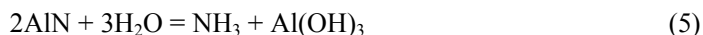
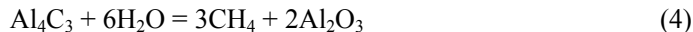
Water reacts exothermally with SPL, and the reaction rate increases with increasing temperature. This can be observed if the pot is watered before it is dug out. The reaction often becomes violent, and large amounts of gases are evolved. Weathered SPL will disintegrate as it is aged. Recognizing that SPL contains some Al and Na metal, the reactions between SPL and water are:



Or as wet SPL is inherently basic:



Other reactions are:



Due to the last reaction, a smell of ammonia is often observed during cell autopsy. The evolution H_2 and CH_4 makes SPL potentially explosive and on 19 March 1990, a ship carrying SPL exploded in Port Alfred, Quebec, Canada, killing two people and causing 30 M\$ damage.

3. Treatment of SPL

The poisonous and potentially explosive properties of SPL make it necessary to use special precautions in order to transport it from a smelter to a treatment site. In some instances a “detoxification” process is applied at the smelter in order to reduce transport costs. Another difficulty is the variation in composition. The variations in the two critical components are: fluorides 10 – 18 wt% and cyanides 700 – 4500 ppm [2].

Many unsuccessful processes and patents for treatment of SPL have been published. Some got as far as trial production but were then stopped. This paper will, however, concentrate on the methods which are in use or potential new methods.

3.1 Landfill

More than 50 % of the produced SPL is landfilled without any special treatment. 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 poisoning 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 cleaning. Storage in a basin on the seashore was an earlier practice in Norway and Iceland. The cyanides were oxidized in a basin and possible runoff of fluorides are not a poison in seawater. A study in Iceland found no ill effect on the marine environment. The practice has, however, been stopped. Today Hydro landfill the SPL in a former limestone quarry on an island in the Oslo fjord. The site will, however be filled up in 2022.

3.2 Use of SPL in other Industries.

Addition to cement has been the most successful use of SPL in other industries (Figure 2) [3]. The carbon part has caloric value and can be used as fuel substitute mixed with coal. The refractory part is a source of SiO_2 and Al_2O_3 . Fluorides are beneficial to the clinker reaction, Equation (6), so that the cement process may run at a slightly lower temperature. The cyanides are destroyed at the cement process temperature.



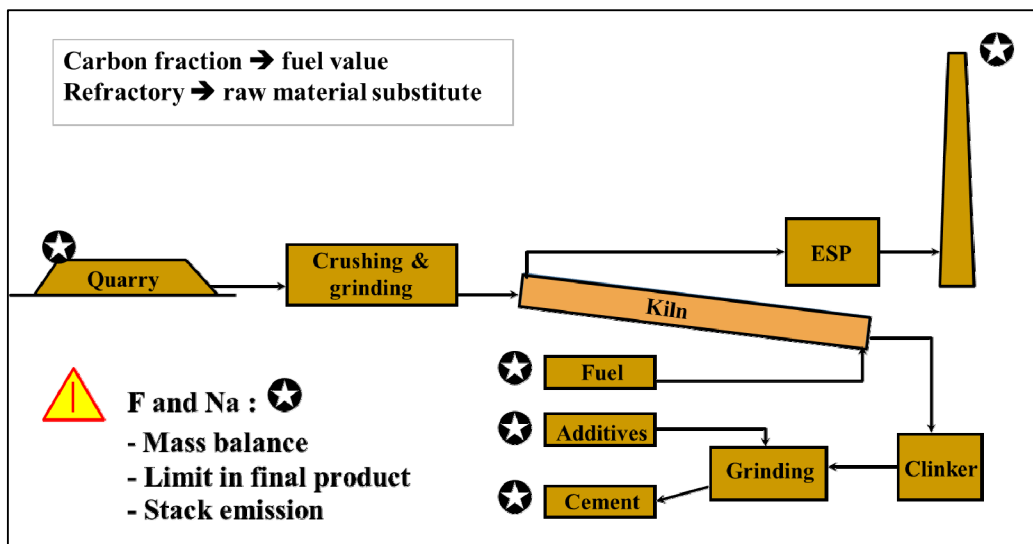


Figure 2. Flowsheet of re-use of SPL in cement production (redrawn from [3]). ESP is Electrostatic Precipitator. Fluor and Na need attention as for the limit in the final product and stack emissions; a full mass balance of these two elements is recommended.

The sodium in the spent potlining is a problem, however. Some cement factories want to produce low sodium cement and may not want to add extra sodium. Generally a typical addition of SPL to cement is 0.2 %. It is also wanted to have the composition as even as possible and without any aluminium metal particles. Such particles are deleterious in the finished cement. There is also some uncertainty in the industry about any long term effect. Addition to cement is carried out in France, Russia, Brazil and South Africa.

SELCA ECOINDUSTRY in Italy has used First cut as an additive in steelmaking. The fluorides will improve slag formation and can substitute for CaF_2 addition. Use of SPL in steelmaking has been tried in Russia, China, United States and Brazil but the present amounts treated are believed to be small. The process diagram is shown in Figure 3. Problems are variability in composition. Sizing is critical.

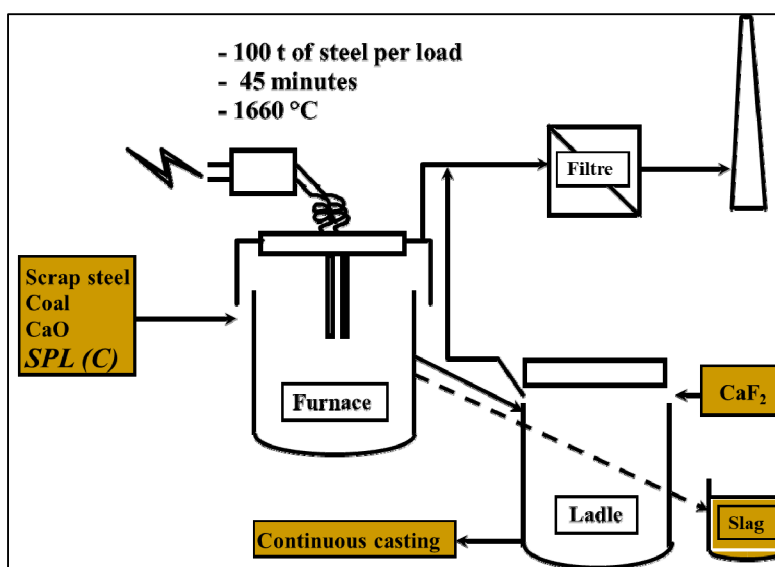


Figure 3. Use of SPL in steelmaking (redrawn from [3]).

Regain [4] has processed more than 250 000 tons of SPL from smelters in Australia. They carry out a detoxification process at the plant. The material is first crushed and classified. The reactive materials are leached with water and the evolved H_2 and CH_4 gases are used partly for a heat treatment to destroy the cyanides. The material is then no longer hazardous and can be shipped around the world for further treatment by cement, brick and steel plants.

Other uses are in brick manufacture (Brazil) or adding first cut or untreated SPL to rock wool (Norway, France and Germany).

3.3. Pyrometallurgical SPL Processes.

Reynolds, later Alcoa, developed a detoxification process where a blend of presized SPL, limestone and an antiagglomeration agent are calcined in a rotary kiln using natural gas as the heat source. The concept is that CaO will convert $NaF-AlF_3$ to CaF_2 which is much less soluble. The cyanides are destroyed by the process. The capacity is 109 000 t/year. The product was delisted by EPA, US, as hazardous waste in 1991, but the delisting was repealed in 1997. The reason was that the real leachability of fluorides was higher than demonstrated by the used American test. The test used one single leaching for 18 hours with acetic acid. This test gave an unrealistic low leachability due to buffering of the alkaline SPL. A French test [3] which used distilled water with 3 consecutive leachings for 16 hours gives a much higher leachability, see Figure 5. In lack of better processes the Reynolds process with a controlled landfill is still in operation.

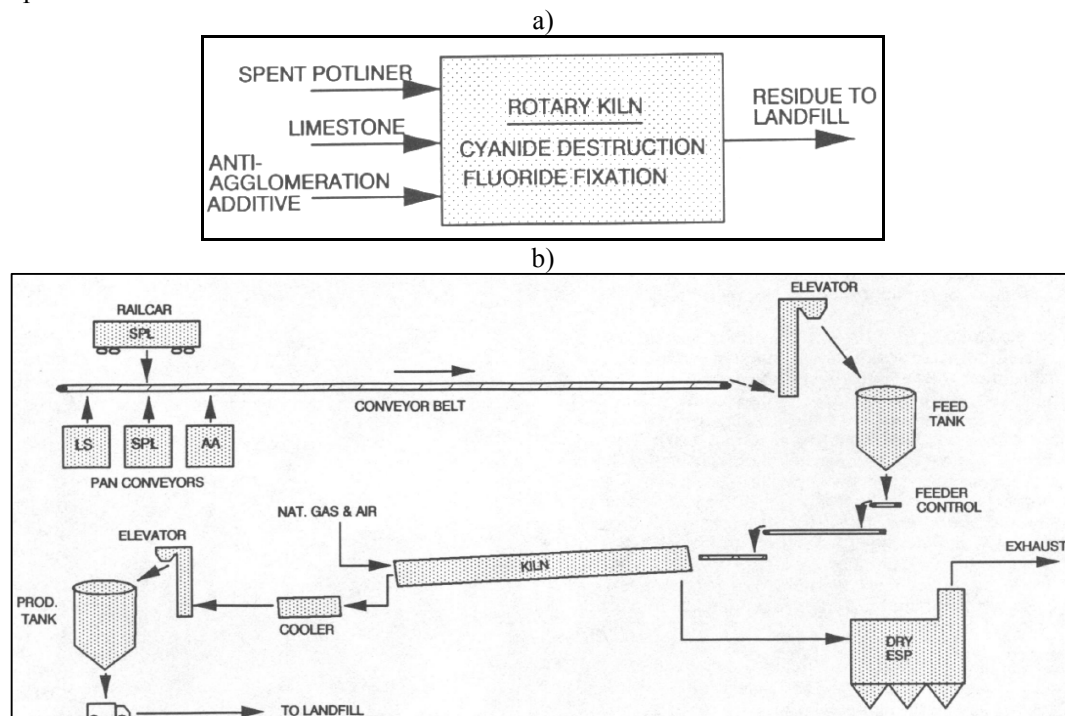


Figure 4. The Reynolds process. a) Process concept. b) Process schematics [5].

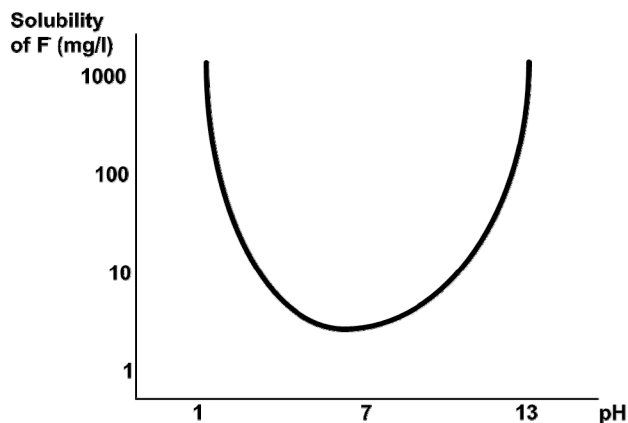


Figure 5. Solubility curve of fluorides [6].

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 aluminium electrolysis. The process was tried in a full size smelting furnace, but has now been stopped.

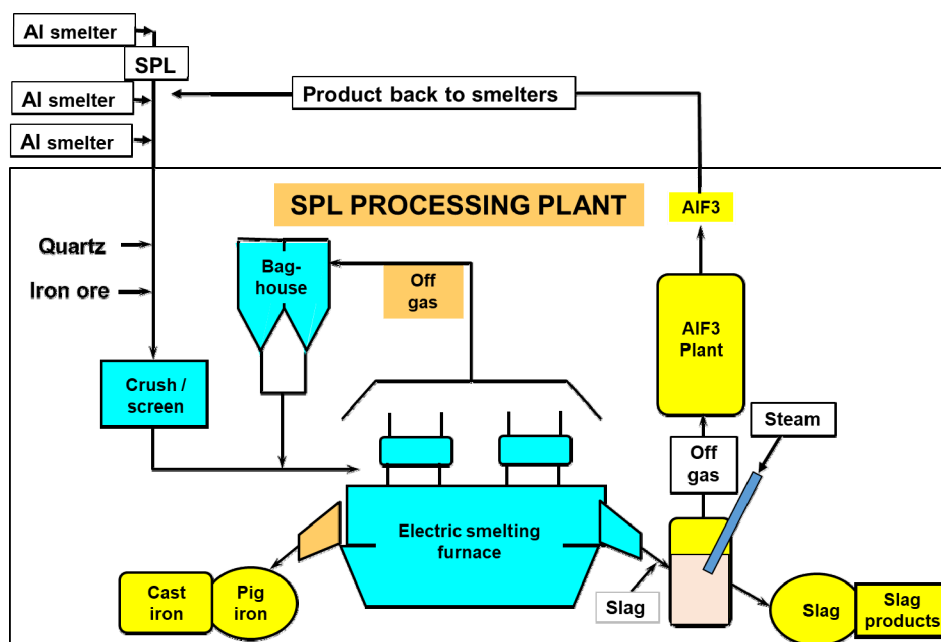


Figure 5. Elkem electric furnace process (redrawn from [3] and [7]).

The company Tetronics, UK [8] has announced that they have a robust plasma treatment for spent potlining. It is a single stage with minimal pretreatment. They will recover fluoride and energy - using the calorific value of carbon in the process. The remaining waste is then converted into an inert non-hazardous vitrified material. They propose to carry out the process at the smelter to avoid expensive transport.

Plasma process with vacuum distillation at 1300 °C and vaporization of fluorides is also under development in China.

3.4. Aqueous Processes for Treatment of SPL.

Alcan, now Rio Tinto, has developed the so-called LCL&L (Low Caustic Leaching & Liming) process [9]. The first step is handling and storage in SPL containers. The SPL is ground (less than 300 μm) by an air-swept autogeneous mill with air classification and screening to a ground SPL storage. The wet sector consists of leaching steps, first with water to extract soluble fluorides and most of the cyanides followed a low caustic to extract the remaining cyanides and fluorides. Carbon and insolubles are filtered out. The filtrate is treated in a pressurized reactor at 180 °C to destroy the cyanides. The liquor after cyanide destruction is concentrated by evaporation and NaF is precipitated out. The remaining liquor is used in an adjacent Bayer plant. NaF may be converted to the less leachable CaF_2 by reaction with lime.

The plant was started in 2008 and reached full capacity in 2014 with treatment of 80 000 tons/year and produces 94 000 tons CBP (70 % SiO_2 and Al_2O_3 , 30 – 40 % C), 48 000 tons FBP (CaF_2 and or NaCl), 30 000 tons caustic solution (27 % NaOH). The CBP contains five times less total fluorides and sodium which allows higher doses if added to cement production. The carbon has a calorific value. The FBP can be used as an alternative raw material for AlF_3 production. The caustic liquor is used in the Bayer process for Al_2O_3 production.

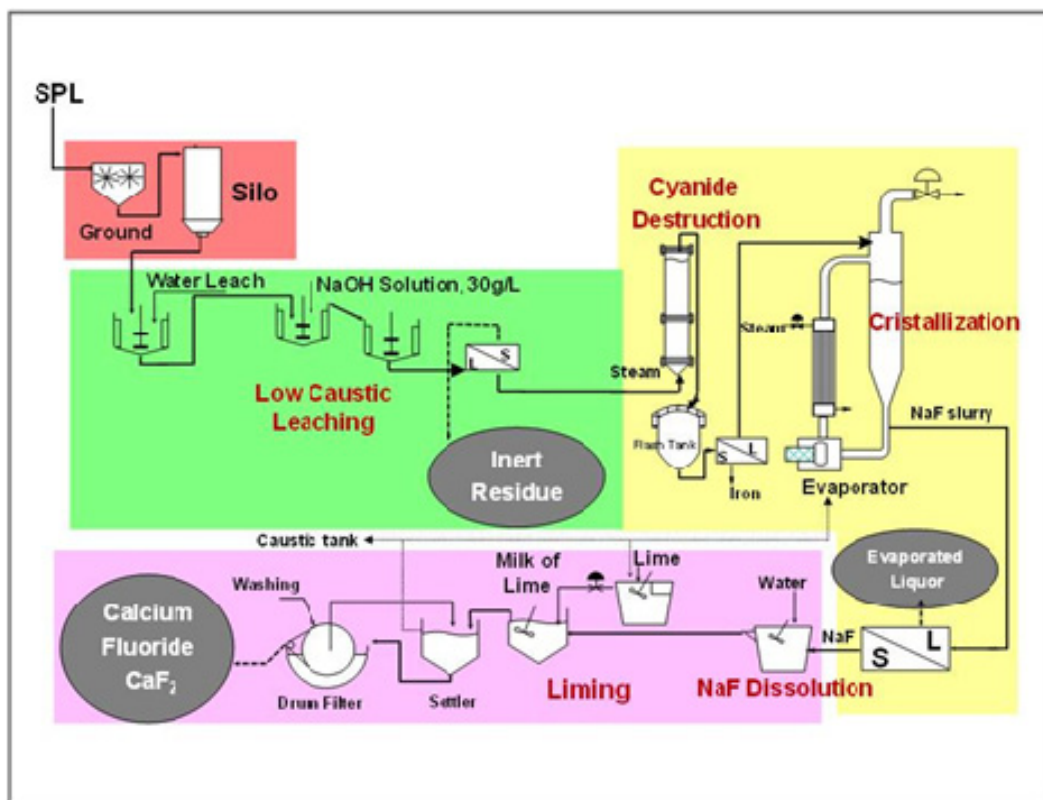


Figure 6. Simplified flow sheet for the LCL&L process [9].

4. Final Discussion

China is producing nearly 55 % of the world aluminium but accounts on industrial processes for SPL treatment is very limited. In the abstract of a paper from Li Nan et al from Kunming University they state in 2013 [10]:

“The research on recycling aluminium-electrolysis spent potlining (SPL) and the industrial application was introduced. At present most of the recycling ways, which particularly stresses on environmental protection and did not pay comparative attention to economic benefits, were still studied in the laboratory rather than applied to industry The only reported industrial application is “ Researching on detoxification SPL, an industrial application technology”, which was invented by Zhengzhou Light Metals Research Institute(CHALCO)”.

Chalco SPL treatment process diagram is shown in Figure 7 [11]. It is a pyro-process; the process temperature is 900 – 1050 °C, which destroys all cyanides rapidly. The detoxified solid residue is recycled to cement production and the fluorides to an alumina scrubber.

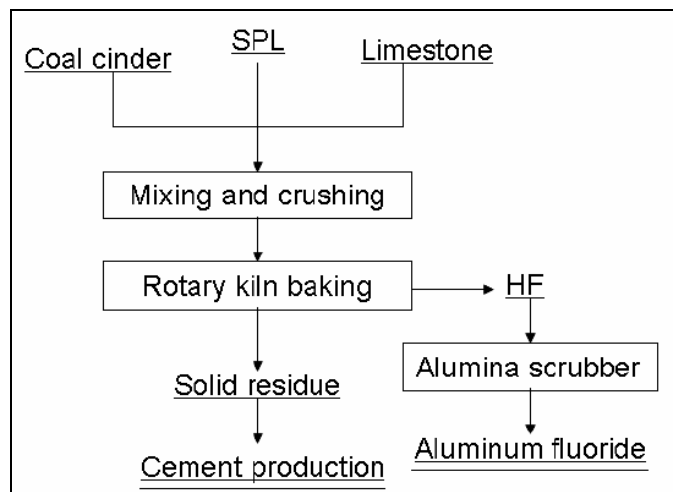


Figure 7. Chalco SPL treatment process.

There are also some reports on small scale flotation processes, but it is assumed that landfill is the main procedure for handling of SPL in China.

In the West today, 3 processes for SPL treatment are used on a reasonably large scale, apart from landfilling:

1. The Reynolds process calcining SPL with limestone.
2. Addition to a cement calciner with or without pretreatment.
3. The aqueous LCL&L process.

The Reynolds process has problems with fluoride leakage from the product and cement addition may get into problems due to the sodium content. The LCL&L process appears to be satisfactory, but it needs to be close to a Bayer plant.

In the West about 50 % of SPL is still landfilled or stored. It appears that the industry is still waiting for a fully satisfactory process.

In my opinion, a pyrometallurgical process will be the best solution. Tetronics claim to have a satisfactory plasma process. The Elkem cast iron process could be close to perfect. Cyanides are destroyed, the calorific content of the carbon is utilized, a useful byproduct is produced (cast iron) and the fluorides are contained in a glassy phase with low leachability. It is a pity that further work was stopped.

5. References

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