# **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 consist 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 potlining(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 potlining (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<sub>4</sub>C<sub>3</sub> 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:

$$2AI + 3H_2O = 3H_2 + AI_2O_3$$
(1)

$$2Na + 2H_2O = H_2 + 2NaOH$$
(2)

Or as wet SPL is inherently basic:

$$2AI + 2NaOH + 2H_2O = 3H_2 + 2NaAIO_2$$
(3)

Other reactions are:

$$Al_4C_3 + 6H_2O = 3CH_4 + 2Al_2O_3$$
(4)

$$2AIN + 3H_2O = NH_3 + AI(OH)_3$$
<sup>(5)</sup>

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.

$$CaO + 2 CaO \cdot SiO_2 = 3CaO \cdot SiO_2$$
(6)

### 5. References

- 1. W.S. Rickman, Circulating bed combustion of spent potlining, *Light Metals* 1988, 735-743.
- 2. George Hollywell and Raymond Breault, An overview of useful methods to treat, recover, or recycle spent potlining, *JOM 65*, No11 (2013), 1441-1451.
- 3. Michel Reverdy and Pierre Personnet, Lecture at *The International Course on Process Metallurgy of Aluminium*, Trondheim, Norway (1998).
- 4. Regain Processing Technology, <u>http://www.regainmaterials.com/aluminium-smelting-industry/regain-spl-solution/spl-processing-technology</u>, retrieved on 8n August 2017
- 5. Dennis G. Brooks, Euel R. Cutshall, Donald B.Banker and Dennis F.Strahan, Thermal treatment of spent potlining in a kiln, *Light Metals* 1992, 283-287.
- 6. Michel Reverdy and Pierre Personnet, Lecture at *The International Course on Process Metallurgy of Aluminium*, Trondheim, Norway (2000).
- 7. B. Høgdahl, R. Ystebø and F. Fereday, *Report "Elkem SPL Recycling Process*, February 1994.
- 8. Tetronics website: <u>http://tetronics.com/our-solutions/hazardous-material-</u> <u>treatment/spent-potliner/</u>, retrieved on 7 August 2017.
- Laurent Birry, Stéphane Poirier and Simon Leclerc, The LCL&L process: A sustainable solution for the treatment and recycling of spent potlining, Proceedings of 34<sup>th</sup> Internationqational ICSOBA Conference, Quebec City, Canada, 2 – 6 October 2016, Travaux 45, 705-712.
- Li Nan et al, The recycling and industrial application of aluminum electrolysis spent pot-lining in China, *Carbon Techniques* (2013 – 03). Abstract only on: <u>http://en.cnki.com.cn/Article\_en/CJFDTotal-TSJS201303018.htm</u>, retrieved on 7 August 2017.
- 11. Wangxing Li, Xiping Chen, Development status of processing technology for spent potlining in China, *Light Metals* 2010, 859-861.