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.

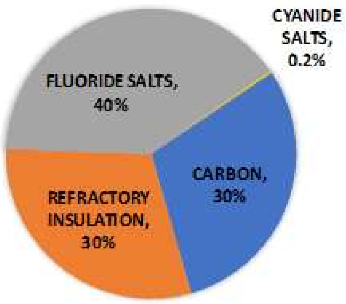

Figure 1. General composition of SPL (from Rickman [1]).

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° (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° 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).

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.