SPL and Red Mud: Value Creation from Hazardous Wastes

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Abstract



Spent pot lining (SPL) and red mud are well-known waste products from the aluminum industry and have been the cause of significant spending for all aluminum producers. The SPL generation rate is approximately 1 to 1.5 million tonnes per annum, representing a significant environmental burden to the aluminum industry. Previous reports indicated that more than half of the total amount of SPL generated is stored in lined or unlined sites or buildings, waiting for further treatment. Similarly, for every tonne of alumina refined, approximately 1 - 1.5 tonnes of red mud is generated. While disposal and storage options exist, there is a clear and present need for better ways in managing wastes from the primary aluminum industry. At the University of Toronto, the Process Metallurgy Research Labs in collaboration with Dastur Innovation Labs are working extensively to understand the chemistry of SPL and red mud and extract value out of these wastes. Some of the potential values of SPL are: (a) as a flux in the non-ferrous industry (b) as an alternate to coal in ironmaking blast furnaces and (c) as a carbon injection source in the electric arc furnace (EAF). The value of red mud can be realized as a flux for the more efficient desulphurization and dephosphorization of steel, which saves the steel industry significant costs by reducing process times. Experimental and simulation techniques along with economic assessments have been performed to test these ideas, and the results and feasibility are discussed in detail.

Keywords: SPL, red mud, waste to value, experiments, simulation.

1. Introduction

Spent pot lining (SPL) is a by-product of the aluminum industry, obtained from the used Hall-Héroult electrolytic cells. A typical Hall-Héroult cell is schematically shown in Figure 1 below [1]. Due to a very high melting point of alumina (2045 °C), it is dissolved in cryolite (Na₃AlF₆) to lower its melting point to 970 °C. Molten alumina is then reduced electrochemically with carbon electrodes via the following reaction:

$$C(s) + 2O^{2-}(l) \rightarrow CO_{2}(g) + 4e^{-} \dots \text{ oxidation at anode}$$

$$Al^{3+}(l) + 3e^{-} \rightarrow Al(l) \dots \text{ reduction at cathode}$$
(1)

$$2Al_2O_3(l) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$
⁽¹⁾

During the electrolysis process, other products are also formed due to diffusion of fluorides into carbon cathode blocks, leakage of air into the bath, or absorption of the electrolyte into the refractory lining. These reactions, along with the consumption of the carbon electrodes, lowers the overall cell efficiency, necessitating cell replacement after 5 to 8 years [1]. While the outer steel shell can be reused, the remaining cell material comprising of solidified electrolyte, refractory lining and electrodes, known as spent pot lining (SPL), is usually discarded. The material above the collector bar (depicted in Figure 1) comprises mostly of carbonaceous components and is referred to as 1st cut SPL, whereas the material below comprises mainly of refractory silicates and is referred to as 2nd cut.



Figure 1. Schematic of a typical Hall-Héroult Cell [1].

Figure 2. Global production of primary aluminum (based on [20]) and SPL (calculated).

SPL is classified as a hazardous waste material in 1988 by the U.S. Environmental Protection Agency (USEPA) [2, 3] and as a special waste in Canada [4] due to the presence of leachable cyanides and fluorides. The compositions of SPL vary widely [2, 4-6, 7-19], on account of variation in the cell lining components, dismantling procedures, and time under operation.

The production of global primary alumina increased from 40 to 60 Mtpa during the time period of 2007 - 2016 [20]. Considering approximately 25 kg of SPL generation per ton of primary aluminum produced [8], the global SPL generation rate can be approximated to have risen from 1 to 1.5 Mtpa during the same time period. This presents a significant environmental burden to the aluminum industry. The variation of primary aluminum production and approximated SPL generation rates is depicted in Fig. 2. The current SPL disposal options are as follows:

- a) Secured landfills which require costly remediation [10],
- b) Use as a feedstock for other industries (e.g. steelmaking [18, 21], mineral wool industry),
- c) Fluidized bed combustion [17]
- d) Pyrohydrolysis and pyrosulfolysis [2]
- e) Fuel in aluminum cast house burners [22]

capacity. Further innovation in utilizing SPL and red mud as value-added byproducts rather than hazardous waste streams to be mitigated will allow for the aluminum industry to obtain forward momentum and become a more sustainable industry. Future work includes the development of AlF_3 crystals from SPL for medical drug applications and also ways to remove fluorides from SPL to avoid the detrimental of sooty NaF during combustion applications.

7. References

- 1. George Holywell, Raymond Breault, An overview of useful methods to treat, recover, or recycle spent potlining, *Journal of the Minerals, Metals and Materials Society* 2013 65, 1441–1451.
- 2. B.I. Silveira et al., Characterization of inorganic fraction of spent polliners: evaluation of the cyanides and fluorides content, *Journal of Hazardous Materials*, 89 (2002), 177-183.
- 3. W.K. O'Connor, P.C. Turner, G.W. Addison, Method for processing aluminum spent potliner in a graphite electrode arc furnace, The United States of America as represented by the United States Department of Energy, 2002.
- 4. George Holywell, Raymond Breault, An overview of useful methods to treat, recover, or recycle spent potlining, *JOM*, 65 (2013), 1441-1451.
- 5. Bjørn Moxnes et al., Addition of refractories from spent potlining to alumina reduction cells to produce Al-Si alloys, *Light Metals* 2003, 329-334.
- I. Rustad, K.H. Karstensen, K.E. Ødegard, Disposal options for spent potlining, J.J.J.M.G. G.R. Woolley, P.J. Wainwright (Eds.) *Waste Management Series*, Elsevier, 2000, 617-632.
- 7. N. Li, G. Xie, Z. Wang, Y. Hou, R. Li, Recycle of spent potlining with low carbon grade by floatation, *Advanced Materials Research*, 881-883 (2014), 1660-1664.
- 8. Paulo Von Krüger, Use of spent potling (SPL) in ferro silico manganese smelting, *Light Metals* 2011, 275-280.
- 9. D. Mikša, M. Homšak, N. Samec, Spent potlining utilisation possibilities, *Waste Management & Research*, 21 (2003), 467-473.
- 10. T.K. Pong et al., Spent Potlining A Hazardous Waste Made Safe, Process Safety and Environmental Protection, 78 (2000), 204-208.
- 11. T. Hopkins, P. Merline, Comtor Process for Treatment of Spent Potlining, *Mineral Processing and Extractive Metallurgy Review*, 15 (1995), 247-255.
- 12. J.G. Lindkvist, T. Johnsen, Method for treatment of potlining residue from primary aluminium smelters, *Elkem Technology*, 1994.
- 13. K.W. Grieshaber, C.T. Philipp, G.F. Bennett, Process for recycling spent potliner and electric arc furnace dust into commercial products using oxygen enrichment, *Waste Management*, 14 (1994), 267-276.
- 14. D.B. Banker et al., Detoxification of aluminum spent potliner by thermal treatment, lime slurry quench and post-kiln treatment, *Reynolds Metals Company*, 1992.
- 15. Rudolf P. Pawlek, Spent potlining: water soluble components, landfill and alternative solutions, *Light Metals* 1993, 399-405.
- 16. O.M. Gardner, R.L. Cheek, Treatment of aluminum reduction cell lining combined with use in aluminum scrap reclamation, *Imco Recycling Inc.*, 1990.
- 17. B.C. Kim et al., Laboratory feasibility studies for the fluidized-bed combustion of spent potlining from aluminum reduction, *United States Environmental Protection Agency*, 1984.
- 18. D.R. Augood, R.J. Schlager, Potlining flux in making steel, *Light Metals* 1983, 1037-1043.
- 19. R.E. Hurt, Spent potliner compositions and generation rates, *Proceedings of the Workshop on Storage, Disposal and Recovery of Spent Potlining*, Environmental Committee, Aluminium Association, 1981.

- 20. Primary Aluminium Production, International Aluminium Institute, 2018.
- 21. Bruna Meirelles, Henrique Santos, Economic and environmental alternative for destination of spent pot lining from primary aluminum production, *Light Metals* 2014, 565-570.
- 22. D. Yu, V. Mambakkam, A. H. Rivera, D. Li and K. Chattopadhyay, Spent Potlining: A myriad of opportunities, *Aluminium International Today* 2015, 5-7.
- 23. Rudolf P. Pawlek, Spent Potlining: an Update, *Light Metals* 2012, 1312-1317.
- 24. <u>www.factsage.com</u>
- 25. Albert Einstein, Eine neue Bestimmung der Molekuldimensionen, *Ann. Phys.*, 19, 1906, 289-306.
- 26. P. Toscano, T.A. Utigard, Nickel, copper, and cobalt slag losses during converting, *Metallurgical and Materials Transactions B*, 34B (2003), 121-125.
- 27. D. Yu, and K. Chattopadhyay, Enhancement of the nickel converter slag-cleaning operation with the addition of spent potlining, *International Journal of Minerals, Metallurgy, and Materials,* (2018) 25, 881-xxx. https://doi.org/10.1007/s12613-018-1637-0.
- 28. <u>http://www.cfd.com.au/cfd_conf15/PDFs/098LIA.pdf</u>
- 29. L. Gao et al., Using SPL (spent pot-lining) as an alternative fuel in metallurgical furnaces, *Metallurgical and Materials Transactions E* (2016) 3, 179, https://doi.org/10.1007/s40553-016-0085-x.
- 30. V. Mambakkam, Spent Pot Lining in lieu of EAF Carbon Injection, BASc. Thesis, Department of Materials Science and Engineering, University of Toronto, 2018.
- 31. Fengshan Li, Yanling Zhang, and Zhancheng Guo, Experimental study on hot metal desulfurization using sintered red mud-based flux, *JOM*, Vol. 69, No. 9, 2017, DOI: 10.1007/s11837-017-2454-z.