Considerations for Dealing with Spent Potlining
Technical Paper for 11th Australasian Aluminium Smelting Technology Conference

Bernie J Cooper, Regain Technologies Pty Ltd, Australia

Abstract

The carbon cathode and refractory lining material that is removed from the electrolytic cells (or pots) used in primary aluminium smelting is known as spent potlining (SPL). SPL is hazardous waste material subject to close regulatory control in most jurisdictions and its disposal has proven to be a challenge for the aluminium industry. This paper sets out considerations for dealing with SPL. A review of the chemical reactions that take place during the typical operational life of the lining leads to an overview of the chemical composition of the resultant SPL material and its inherent hazards. Potential safety and environmental risks associated with the SPL hazards are discussed. Issues to be addressed in using SPL as input to downstream industrial processes are examined using cement manufacture as a case study. Life cycle analysis is used to support an approach to optimising the economic use of all of the SPL material thus ensuring its safe and effective disposal.

Keywords: Spent potlining, Aluminium smelting, Hall-Heroult process, Fluoride, Cyanide, Hazardous waste..

Introduction

Production of primary aluminium metal with the Hall-Heroult process involves electrolytic reduction of alumina in cells or pots. The electrolyte is made up of molten sodium aluminium fluoride (cryolite) and other additives and is contained in a carbon and refractory lining in a steel potshell. Over time, the effectiveness of the lining deteriorates and the lining of the pot is removed and replaced. The lining material that is removed from the pots is known as spent potlining (SPL).

SPL reacts with water with reaction products that are potentially combustible or explosive [1]. SPL also presents environmental concerns due to the presence of cyanide and soluble fluoride salts. In 1988 the United States Environmental Protection Authority formally listed SPL as a hazardous waste [2]. Sørlie and Øye [1] refer to environmental agencies in an increasing number of countries defining SPL as a hazardous material. Pawlek [3] noted that about 25kg of SPL results from each tonne of aluminium metal produced and that while, in the past, most of the SPL has gone to landfill, this practice must change if the industry wants to claim a reasonable degree of sustainability and environmentally tolerable emissions.

There has been substantial research and development of methods to treat SPL rather than landfill. Drawbacks of many methods of treating SPL are that not all of the SPL can be treated and/or there are residual materials without ready disposal options other than landfill. SPL is rich in substances that have beneficial energy saving and greenhouse gas (GHG) emission reduction properties when used in industries such as cement manufacture. These industries are faced with increasing energy costs and societal expectation of reduction in GHG emissions [4] [5]. The cement industry can make use of SPL without producing residual materials. However realisation of the potential benefits has been limited by a number of factors including adverse effects on downstream processes when trying to use SPL, the hazards associated with SPL and the regulatory constraints associated with SPL [6] [7] [8].

Chemical Reactions During the Life of the Pot Lining

Over the typical life of a pot (three to ten years), materials infiltrate the cathode lining and cause it to deteriorate. Øye [6] makes the observation that there is complex chemistry in the pores in the carbon. Sørlie and Øye [1] and, also, Hop et al [9] provide an appreciation of the type and complexity of the chemical reactions that take place in the linings of an aluminium reduction cell over the life of the linings and describe the mechanism by which the lining is progressively penetrated by aluminium metal, sodium metal and the sodium aluminium fluoride/sodium fluoride electrolyte.

Chemical reactions result in the formation of various carbides, nitrides and cyanides within the pot linings (e.g. refractory lining, carbon cathode, carbon sidewalls). Indicative examples of the chemical reactions are:

- reaction of cryolite with nitrogen and sodium to form nitrides e.g.
  $Na_3AlF_6 + 0.5N_2 + 3Na \rightarrow AlN + 6NaF$

- metals such as aluminium react with carbon to form carbides e.g.
  $4Al + 3C = Al_4C_3$

- various carbon-nitrogen compounds are also produced in the forms of cyanides e.g.
  $1.5N_2 + 3Na + 3C \rightarrow 3NaCN$ [1].

Nepheline and albite are formed as a sodium fluoride as the molten electrolyte reacts with the refractory lining. Examples of these reactions are:

- nepheline from refractory reaction at low SiO_2 / Al_2O_3 ratios e.g.
  $6NaF + 3SiO_2 + 2Al_2O_3 \rightarrow 3NaAlSiO_4 + Na_3AlF_6$

- albite from refractory reaction at high SiO_2 / Al_2O_3 ratios e.g.
  $6NaF + 9SiO_2 + 2Al_2O_3 \rightarrow 3NaAlSi_3O_8 + Na_3AlF_6$ [1].

Properties of SPL

When the linings are removed from the pot they contain substantial amounts of sodium aluminium fluoride and sodium fluoride. The resultant SPL also contains aluminium metal, sodium metal, carbides, nitrides and cyanides. SPL readily absorbs atmospheric water (humidity), which reacts with a number of these components. Sørlie and Øye [1] identify the following as typical chemical reactions of the metals or chemical compounds with water

- Aluminium metal to hydrogen $\quad 2Al + 3H_2O \rightarrow 3H_2 + Al_2O_3$

- Sodium metal to hydrogen $\quad 2Na + 2H20 \rightarrow H2 + 2NaOH$

- Aluminium carbide to methane $\quad Al_4C_3 + 6H_2O \rightarrow 3CH_4 + 2Al(OH)_3$

- Ammonia from aluminium nitride $\quad 2AlN + 3H_20 \rightarrow 2NH_3 + Al_2O_3$.

SPL is particularly hazardous due to:
- Its propensity to combine with water and generate explosive gases
- Presence of leachable cyanide
- Presence of leachable fluorides [1] [10] [11] [12].

SPL is classified as hazardous waste material in many regulatory jurisdictions and transfer across international boundaries is subject to control under the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal [12].

In its raw form, SPL varies in size from fine dust to lumps of up to one metre (Figure 1). It is typically chemically heterogeneous presenting a wide range in mineral and chemical composition as different materials in the pot lining are mixed together.

Table 1 sets out analysis of SPL based on progressive sampling of SPL from four smelters in Australia between 2002 and 2014.

Table 2 sets out an indication of the relative content of phases present in recovered SPL based on x-ray diffraction (XRD) analysis.
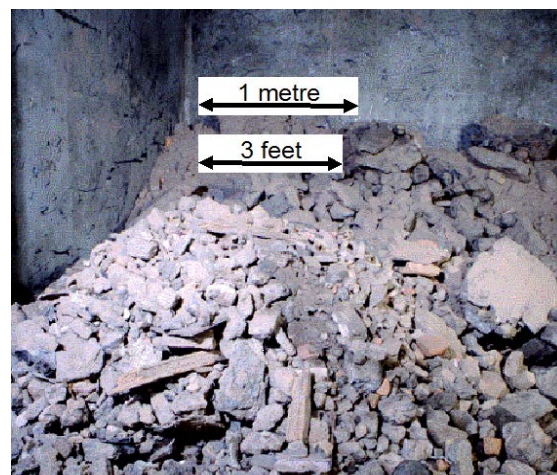

Figure 1 – Raw SPL

Table 1 – Range of Chemical Analysis of Recovered SPL

Description			Carbon Lining	Refractory Lining
Carbon		%	30 to 50	2 to 10
Silicon	as SiO_2	%	2 to 15	10 to 40
Iron	as Fe_2O_3	%	2 to 4	1 to 6
Aluminium	as Al_2O_3	%	10 to 30	15 to 30
Calcium	as CaO	%	1 to 5	1 to 5
Magnesium	as MgO	%	0 to 2	0.5 to 2.5
Sodium	as Na_2O	%	3 to 25	5 to 30
Potassium	as K_2O	%	0.2 to 1	0.5 to 1.5
Fluorine	as F	%	5 to 15	5 to 15
Cyanide		mg/kg	100 to 4,000	100 to 1,500

Table 2 – Indicative Composition based on XRD Analysis of Recovered SPL

Phase			Carbon Lining	Refractory Lining
Beta-Alumina	$NaAl_{11}O_{17}$	%	2	5
Corundum	Al_2O_3	%	5	5
Cryolite	Na_3AlF_6	%	15	15
Villiaumite	NaF	%	15	15
Gibbsite	$Al(OH)_3$	%	4	2
Nepheline	$Na_3Al_4Si_4O_{16}$	%	1	15
Albite	$NaAlSi_3O_8$	%	not detectable	1
Quartz	SiO_2	%	1	3
Fluorite	CaF_2	%	2	2
Other crystalline		%	5	5
Amorphous		%	50	32

Note that the phases present in SPL vary substantially depending on pot lining technology and other factors. The results shown in this table represent an indication of the relative order of magnitude of selected phases typically present in SPL.

Disposal Options for SPL

In the past most SPL has gone to landfill [3]. Current industry practice includes placement of SPL in secure landfills or in storage at or near aluminium smelter sites. There are potential environmental liabilities if leachate from landfills escapes to the environment. For this reason, landfilling of unreacted SPL is prohibited in many regulatory jurisdictions. Godin et. al. [13] describe a study aimed at identifying a site remediation option that would minimise overall environmental impacts for a landfill containing 100,000 cubic metres of SPL. The study was based on a comparative lifecycle assessment (LCA) and modelling of contaminant transport in groundwater. The study makes the observation that: a) avoiding environmental impacts by placing the SPL in a secure landfill depended in the assumption that confinement of the waste material would be perfect and b) that if concerns about the quality of the long term confinement are considered, then total destruction of the SPL would be required to avoid adverse environmental impacts.

As alternatives to landfill, various methods for treatment of SPL have been well researched and described in the literature [1] [3] [7] [12]. Drawbacks associated with most methods include one or more of:

- not all of the SPL can be processed (e.g. the carbon SPL can be handled but not the refractory SPL or vice versa)
- the SPL brings unwanted hazards (e.g. where the nepheline in the refractory portion of SPL provides an attractive flux for clay brick making but the concomitant fluorides may present environmental concerns along with health and safety concerns)
- there are residual waste materials without ready disposal options other than landfill.

A notable treatment option that has the potential to beneficially use all of the SPL material with no residue is the use of SPL derived materials in the production of portland cement.

Use of SPL in the Cement Industry

Portland cement production involves two main process stages as follows.

1 Clinkering - calcium carbonate is heated to convert the calcium carbonate to calcium oxide and then to combine with other substances including alumina, iron and silica to produce tricalcium silicate (alite), dicalcium silicate (belite), tricalcium aluminate and calcium aluminoferrite. The process temperatures see the development of a liquid phase referred to as the clinker melt which subsequently cools to make clinker. Alite is the main active ingredient in portland cement clinker [14].

2 Cement manufacture - the clinker is combined with other minerals such as gypsum, limestone, fly ash, natural pozzolan or slag and ground fine to make cement powder. The portion of clinker in cement is called the cement clinker factor. A lower clinker factor means lower overall cost of cement and less embodied energy in the cement.

Certain chemicals in SPL act as fluxes and mineralisers in the cement clinkering process. A flux is a substance that lowers the temperature at which solid materials enter a liquid phase and/or increases the quantity of liquid at a given temperature. A mineraliser is a substance that accelerates reaction rates and promotes the formation of desired materials in the liquid phase of cement clinker or similar materials. This results in a higher quality product with less kiln residence time leading to less energy use and lower GHG emission for processes such as cement manufacture. Of particular interest with respect to SPL are fluorides as mineralisers and sodium as a flux.

Fluoride mineralisation of clinker is a proven method of increasing the reactivity of the clinker and reducing the amount of clinker used per tonne of cement [8]. The mineralisation effect increases the level of alite in the clinker with a corresponding lowering of the proportion of clinker required to produce cement of a given strength i.e. an improvement of the clinker factor. Optimised fluoride mineralisation sees clinker factor improvement in the order of 10% or more. Borgholm et al [15] refer to fluoride mineralisation reducing the clinker content in cement by 15 to 20% without affecting performance. Under the right market, raw material and clinkering process conditions, fluoride mineralisation of clinker offers significant economic and environmental benefits.

However, both the clinkering process and final cement quality are sensitive to fluoride. Process problems can be expected if an excess level of fluoride is added and/or of the level of fluoride being added to the clinkering process varies. Fluorides may also affect the setting properties of cement [16]. Hill et al [17] refer to effective mineralisation being achieved with 0.25% addition of fluoride. Johansen and Bhatty [8] provide industrial examples of clinker plants using fluoride for mineralisation by adding calcium fluoride (CaF_2) at rates in the range 0.2% to 1.2% by weight of raw meal with most examples in the order of 0.6%. Given that fluorine as F is approximately half the mass of CaF_2 and the typical raw meal to clinker ratio is 1.6:1 [18], addition rates of fluorine as F in the order of 0.2% by weight of clinker are required to achieve mineralisation without adverse effects of excessive fluoride.

Sodium contributes to the clinker melt through its fluxing properties. It also leads to a beneficially more reactive clinker where the clinker raw materials have low to moderate alkali levels. Sodium can be used to balance the important alkali / sulphur ratio in production circumstances where the clinker plant has excessive sulphur levels (e.g. from using petroleum coke as fuel).

Alkalis such as sodium are volatilised at clinkering process temperatures in the burning zones but condense in cooler parts of the system. This can lead to process problems such as build-ups in ducts, formation of rings in rotary kilns and coatings on kiln liners. Excessive sodium from SPL that is not bound to sulphur can readily lead to problems in the final cement product quality. Alkalis may not be desirable in the cement product because of their impact on the crystal structure and reactivity of tri-calcium aluminate causing changes in setting behaviour of cement and the deleterious alkali-silica reaction with certain concrete aggregates that leads to expansive reactions and serious cracking in concrete [16].

The combined effects of fluoride and sodium when using SPL materials in clinkering see a reduction in operating maximum temperature of the clinker kiln. NO_x is formed in the clinkering process by the oxidation reaction of free nitrogen (N_2) with excess oxygen (O_2) in the kiln. Lower kiln temperatures decrease the generation of NO_x emissions [15] [19]

The key constituents of SPL can contribute to the cement clinkering process in the following ways:
- Alumina is a key ingredient in the chemical process for clinkering
- Carbon provides fuel, thus replacing fuel from other sources
- Calcium is the major ingredient in cement clinker
- Fluoride has a mineralising effect, accelerating the rate of formation of alite and allowing alite to stably form at a lower temperature
- Iron contributes to the chemical process for clinkering

- Silicon is a key ingredient in the chemical process for clinkering
- Sodium has a fluxing effect that contributes to the clinker melt and balances the alkali / sulphur ratio. [14]

Realising the potential benefits with SPL in cement manufacture depends on the following key success factors.
1. Properly addressing the explosive gas and cyanide hazards in SPL and establishing regulatory support for use of the SPL in the particular clinker plant.
2. Ensuring that the raw materials, the clinker process and the market conditions for the cement product are such that there will not be process problems or adverse effects on the cement products, due to excessive alkali or fluorides.
3. A well founded understanding of the effect of the chemicals and minerals in SPL on clinker and cement chemistry and the practical knowledge of what innovations will be required in the clinker plant to make proper use of the SPL materials.
4. Consistent chemical composition of the SPL material fed to the clinker manufacturing process to ensure a predictable and reliable effect on process and clinker chemistry.

Lifecycle Assessment of SPL in Cement Manufacture

A Life Cycle Assessment (LCA) approach in accordance with the International Standard ISO 14044 for Environmental Management – Life Cycle Assessment provides a basis for characterising resource consumption, resource replacement, energy consumption, energy savings and other significant environmental aspects associated with the optimised use of SPL in cement manufacture.

The functional unit for the LCA is one metric tonne of SPL excluding aluminium metal and steel cathode bars. The bounded system to identify and quantify the significant environmental aspects of the use of SPL in portland cement manufacture is shown in figure 2. The system includes:
- Receipt of the SPL from the smelter (excluding removal of the lining from the pots)
- Processing of the recovered SPL including removal of aluminium metal and steel cathode bars and production of a chemically homogeneous material
- Use of the processed SPL in cement manufacture with resultant reduction in energy consumption and GHG emissions.
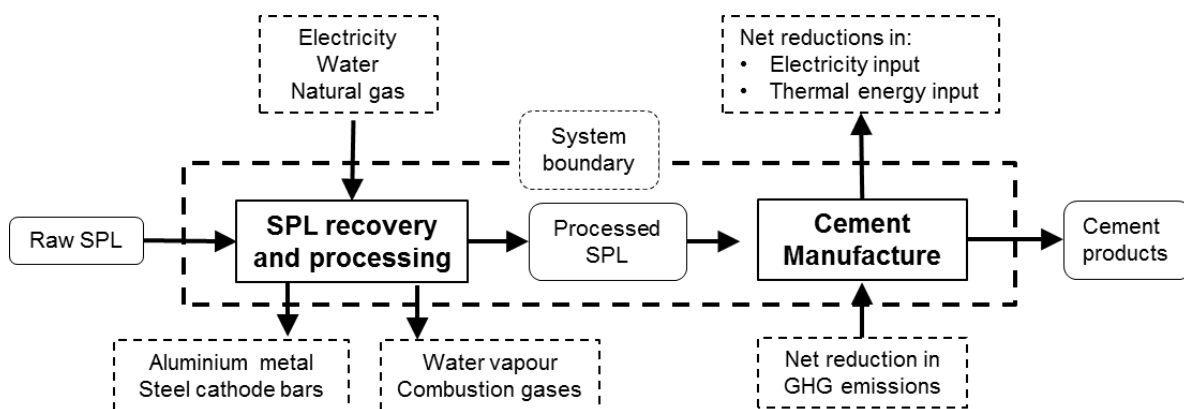

Figure 2 – Lifecycle Assessment System

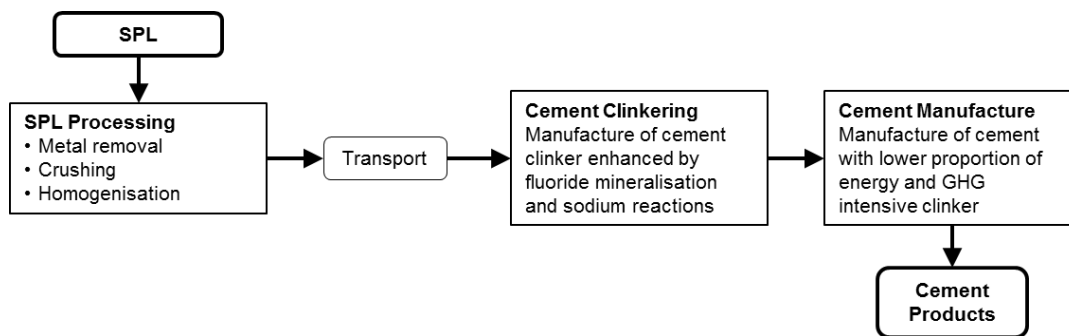Figure 3 depicts a simplified flow diagram showing key process steps.

Figure 3 – Process Flow Diagram

Overall resource consumption and replacement for the LCA system is summarised as follows:

- Metallic materials such as steel cathode bars and aluminium metal are recovered from spent potlining and recycled
- All of the SPL is used in cement clinkering with no residue –
  - carbon replaces coal, gas or petroleum coke fuel
  - alumina, silicon and calcium replace virgin materials
  - fluoride and sodium enhance the clinker process chemistry.

The processing of SPL includes recovery, metal sorting, crushing and homogenising along with chemical processing to remove cyanide and explosive gas hazards such that the resultant processed SPL is safe to handle and use and is not subject hazardous waste regulation. To produce one tonne of processed SPL material in this way and to transport it to adistant cement plant requires in the order of:

- input of 1.5 gigajoules (GJ) of thermal energy
- input of 50 kilowatt hours (kWh) of electrical energy
- emission of 0.2 tonnes of carbon dioxide equivalent (CO_2e)

In order to quantify the significant environmental aspects of the SPL system in the cement clinkering and cement manufacture stages of the process flow set out in figure 3, a scenario of using SPL in a 1 million tonne per year cement clinker plant is considered as follows.

1. Clinker production – 1 million tonnes per year.
2. SPL usage – 20,000 tonnes per year (to obtain optimal mineralisation, the target rate of fluorine addition is 0.20% by weight of clinker with the SPL having a fluorine as F content of 10%).
3. Fluoride mineralisation enabled by the processed SPL material sees improvement in alite level in the clinker of between 5 and 10%.
4. The improvement in alite level sees a reduction in the cement clinker factor and increased cement production of 125,000 tonnes per year. At a clinker factor of 80% the plant can manufacture 1,250,000 tonnes of cement per year from the one million tonnes of clinker. At a clinker factor of 72.7% cement manufacture is 1,375,000 tonnes per year. The result is the extra 125,000 tonnes of cement (10% increase) from the same 1 million tonnes of clinker.

GHG emission from clinker production in a modern and efficient clinker plant is in the order of 850 kg CO_2 per tonne of clinker [20]. The energy required to manufacture clinker is in the order of:

- thermal energy – 3.5 GJ per tonne of clinker
- electrical energy – 80 kWh per tonne of clinker [21].

The 1 million tonne of clinker per year scenario plant produces 1.25 million tonnes of cement. The GHG emission and energy requirements for clinker production per tonne of cement produced are:

- 680 kg CO_2 GHG emission
- 2.8 GJ of thermal energy
- 64 kWh of electrical energy.

Table 3 sets out the energy savings and GHG emission reduction resulting from the gain of an extra 125,000 tonnes of cement production over the base case annual production of 1,250,000 tonnes per year with no marginal energy requirements and GHG emissions.

Table 3 – Annual Energy and GHG Emission Savings for 1 Mtpa Clinker Plant

Environmental Aspect	Basis of Calculation	Net Saving
GHG emission savings from extra production	• base case – 680 kg CO_2 per tonne of cement • net saving = 125,000t x 680 kg CO_2e /t	85,000 t CO_2e
Thermal energy savings from extra cement production with no additional energy	• base case – 2.8 GJ per tonne of cement for the annual production of 1,250,000 tonnes • net saving - 125,000t x 2.8GJ/t	350,000 GJ
Electrical energy savings	• base case – 64 kWh per tonne of cement • net saving = 125,000t x 64 kWh/t	8,000,000 kWh (or 8.0 GWh)

Overall energy consumption, energy savings and GHG emissions associated with the functional unit of one tonne of SPL are summarised in table 4.

Table 4 – Summary of Emission and Energy Aspects for One Tonne of SPL

Description	GHG Emission	Thermal Energy	Electrical Energy
SPL Processing	0.2 t CO_2e	1.5 GJ	50 kWh
Savings from SPL Usage	4.2 t CO_2e	17.5 GJ	400 kWh
Net	**4.0 t CO_2e**	**16.0 GJ**	**350 kWh**

Effective engagement with cement manufacturers and regulators supported with the evidence of the economic and environmental benefits that may be achieved using processed SPL material in cement manufacture has seen new regulatory understanding and a constructive movement in the constraints that may otherwise limit the use of SPL. The result is a sustainable approach to make valuable use of SPL and in a way that there is no residual waste material.

Conclusion

Progressive infiltration of pot linings by electrolyte and other substances sees resultant carbon and refractory SPL materials rich in fluorides and sodium. Certain substances in the SPL

present explosive gas, cyanide and leachable fluoride hazards which mean that SPL is strongly regulated as a hazardous waste.

Changing regulatory conditions facing the primary aluminium smelting industry mean that the past practice of land filling SPL must cease in an increasing number of regulatory jurisdictions. Many treatment methods have been developed as alternatives to landfill, however few methods can use all of the SPL material and many methods result in residual materials for which there is no use.

Making use of SPL in cement manufacture offers an SPL treatment method that can beneficially use all of the chemicals and minerals in SPL with no residual waste material. Fluorides and sodium in SPL material offer particular mineralisation and fluxing properties that are potentially valuable in cement manufacturing given the right set of process and market conditions. However, the clinkering process and cement product quality may be adversely affected by excessive addition of fluorides and sodium. Key success factors for using SPL in cement manufacture are a) establishing regulatory support; b) selecting cement plants with the right raw materials, process and market conditions to make optimal use of SPL; c) knowledge of clinker chemistry and process to support innovation with SPL; and d) chemically consistent SPL material.

Environmental LCA provides a basis for quantifying the economic and environmental benefits available from optimised use of SPL materials in cement manufacture. This information then supports effective engagement with regulators and with cement manufactures.

References

[1]   M. Sørlie and H. Øye, *Cathodes in aluminium electrolysis,* Dusseldorf: Aluminium-Verlag Marketing and Kommunication, 2010.

[2]   B. Silveira, A. Dantas, J. Blasquez and R. Santos, Characterization of inorganic fraction of spent potliners: evaluation of the cyanides and fluorides content, *Journal of Hazardous Materials,* 2002, *89*(2-3), 177–183.

[3]   R. Pawlek, Spent potlining: an update, *Light Metals 2012*, 2012, 1313-1317.

[4]   *Cement roadmap targets – CO2 emission reductions,* The International Energy Agency, 2012.

[5]   R. Köhler , *Energy saving concepts for the European ceramic industry,* European Commission - Intelligent Energy Europe, 2009.

[6]   H. Øye, *Treatment of spent potlining in aluminium electrolysis, a major engineering and environmental challenge,* vol. 5, Centre for Applied Energy Research, University of Kentucky, 1994.

[7]   I. Rustad, K. Karstensen and K. Ødegård, *Disposal options for spent potlining, in* G. Wolley, J. Goumans and P. Wainwright, Eds., *Waste Materials in Construction: Science*

and Engineering of Recycling for Environmental Protection, (Oxford UK: Elsevier Science Ltd, 2000), 617-632.

[8] V. Johansen and J. Bhatty, Fluxes and mineralizers in clinkering process, in J. Bhatty, F. Miller, S. Kosmatka and R. Bohan, Eds., *Innovations in Portland Cement Manufacturing*, (Skokie, Illinois: Portland Cement Association, 2011), 401-438.

[9] J. Hop, T. Støre, T. Foosnaes and H. Øye, Chemical and physical changes of cathode carbon by aluminium electrolysis, *VII International Conference on Molten Slags Fluxes and Salts,*The South African Institute of Mining and Metallurgy, 2004, 775-781.

[10] The Shipowners' Protection Limited, *Flammable gas causes explosion,* London: The Shipowners' Protection Limited, 2010) 18-19.

[11] Transportation Safety Board of Canada - Investigation Marine, *Report of investigation into the circumstances surrounding the explosion on board the Norwegian vessel "Pollux" causing the death of two crew members and injuring twelve other persons on March 19, 1990, at la Baie, Quebec.,* (Transport Canada 1991).

[12] G. Hollywell and R. Breault, An overview of useful methods to treat, recover, or recycle spent potlining, *The Journal of the Minerals, Metals & Materials Society*, *65*(11), 2013, 1441-1451.

[13] Godin, J-F. Ménard, S. Hains, L. Deschênes and R. Samson, Combined use of life cycle assessment and groundwater transport modelling to support contaminated site management, *Human and Ecological Risk Assessment: An International Journal,10*(6), 2004, 1099-1116.

[14] K. Thiesen, E. Jøns and B. Osbæk, Cement clinkering: chemical and physical aspects, *in* J. Bhatty, F. Miller, S. Kosmatka and R. Bohan, Eds., *Innovations in Portland Cement Manufacturing*, Skokie, Illinois: Portland Cement Association, 2011, 365-400.

[15] H. Borgholm, D. Herfort and S. Rasmussen, A new blended cement based on mineralised clinker, *World Cement Research and Development vol. 8*, 1995, 27-33.

[16] J. Bhatty, Role of minor elements in cement manufacturing, in J. Bhatty, F. Miller, S. Kosmatka and R. Bohan, Eds., *Innovations in Portland Cement Manufacturing*, (Skokie, Illinois: Portland Cement Association, 2011) 439-493.

[17] M. Hills, V. Johansen and F. Miller, Solving raw material challenges, *Conference Record of IEEE-IAS/PCA 2002 Cement Industry Technical Conference,* 2002, 139-151.

[18] M. Nisbit, The reduction of resource input and emissions achieved by addition of limestone to portland cement, *Research and Development Serial No 2086,* Portland Cement Association, 1996.

[19] V. Gomes, P. Drumond, J. Neto and A. Lira, Co-processing at cement plant of spent potlining from the aluminium industr*y, Light Metals 2005*, 2005, 507-513.

[20] M. Marceau and M. Van Geem, Lifecycle inventory of portland cement manufacture*,* in J. Bhatty, F. Miller, S. Kosmatka and R. Bohan, Eds., *Innovations in Portland Cement Manufacturing*, (Skokie, Illinois: Portland Cement Association, 2011) 79-114.

[21] N. Madlool, R. Saidur, M. Hossain and N. Rahim, A critical review on energy use and savings in cement industries*, Renewable and Sustainable Energy Reviews 15*, 2011, 2042-2060.