

**THE SPENT POT LINING TREATMENT AND
FLUORIDE RECYCLING PROJECT**

Contact Person

Ken Mansfield

Manager Spent Pot Lining Project

Portland Aluminium

Private Box 1

Portland , Victoria 3305

Australia.

Telephone No 61 3 5521 5550

Facsimile No 61 3 5521 5616

E-mail : ken.mansfield@alcoa.com.au

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FLUORIDE RECYCLING PROJECT**

Authors:

Ken Mansfield, Manager Spent Pot Lining Project, Portland Aluminium
Address Private Box 1, Portland , Victoria 3305, Australia

Gavin Swayn, Spent Pot Lining Area Supervisor, Portland Aluminium
Address: Private Box 1, Portland, Victoria 3305, Australia

Jim Harpley, Spent Pot Lining Senior Process Engineer, Portland Aluminium
Address: Private Box 1, Portland, Victoria 3305, Australia

ABSTRACT

Spent Pot Lining (SPL) is an unavoidable waste product of the electrolytic process in the smelting of aluminium. SPL is considered to be a hazardous waste in various countries because it contains significant quantities of absorbed fluoride along with traces of cyanide.

The disposal of SPL has been primarily in landfill because of difficulties in the development of a successful techno-economic SPL treatment process. Increasing concern about SPL landfilling practices is resulting in regulations in some countries to ban this form of disposal. As a consequence stock piling of SPL is occurring in an increasing number of countries pending the development of a successful treatment process.

In 1992 Portland Aluminium investigated a SPL treatment process based on pyrometallurgical technology and approached a company called Ausmelt in Dandenong, Victoria, Australia, to ascertain if their submerged lance technology furnace process would be suitable to treat SPL. This approach resulted in Portland Aluminium, Alcoa and Ausmelt personnel working together on trials during 1992-1994 in Ausmelt's demonstration furnace to produce a slag and off gases containing hydrogen and sodium fluoride. The trials also evaluated the effect of oxygen enrichment to increase the concentration of hydrogen fluoride and the ability to recycle sodium fluoride particulate produced as the furnace off gases cooled.

Other separate developmental work by Portland Aluminium, using CSIRO, resulted in the production of aluminium fluoride from the offgases from the pyrometallurgical process. The results of these projects influenced Portland Aluminium and Alcoa to authorise up to A\$26 400 000 in December 1995 to construct a Research and Development processing facility to treat SPL at Portland.

The Portland Aluminium unique gas treatment process converts hydrogen fluoride in the furnace offgases to aluminium fluoride in a multistage fluidised bed reactor, designed by Portland Aluminium. The aluminium fluoride produced in the reactor has been trialed successfully in Alcoa's aluminium smelting process as a replacement for imported aluminium fluoride.

The installation in mid 2001 of a slag granulation system has enabled the production of a granulated vitreous slag having leachability qualities that conform to Victorian EPA criteria for the unrestricted use of the granulated vitreous slag from 'The Alcoa Portland SPL Process'. The unrestricted use of the granulated slag successfully completes 'The Alcoa Portland SPL Process' which treats the hazardous waste material SPL and converts it into non hazardous useful products. As at June 2002 over 10,000 tonne of SPL has been successfully processed through the Portland SPL facility.

COMPANY BACKGROUND

Portland Aluminium is a joint venture, which is owned by Alcoa of Australia (55%), CITIC Australia Pty Ltd (22.5%) and Marubeni Australia Ltd (22.5%). The joint venturers own one of the largest aluminium smelters in the Southern Hemisphere located in Portland, Victoria, Australia. The smelter is managed by Alcoa Portland Aluminium Pty Ltd, trading as Portland Aluminium, a wholly owned subsidiary of Alcoa of Australia. Alcoa of Australia Limited is an unlisted public company whose principal shareholders are Alcoa Inc (60 percent) and WMC Limited (39.25 percent). Alcoa is also the owner of the Point Henry aluminium smelter near Geelong and the brown coal mine and power station at Anglesea. The combined annual aluminium capacity of the two smelters is more than 530 000 tonnes with most of it being exported.

In Western Australia Alcoa mines bauxite in the Darling Range south of Perth and refines this material to alumina in its three refineries in the south west region of Western Australia. Alcoa is the world's largest producer of alumina.

SOCIAL AND ENVIRONMENTAL RESPONSIBILITIES

From the outset of the establishment of the Portland Aluminium smelter the social and environmental concerns of its location and operation were of prime significance, and are entrenched as a part of the operating culture of the smelter in its day to day activities.

The social and environmental responsibilities of Portland Aluminium have been illustrated by many actions, some of which are:

- Achieving levels of fluoride emissions that are approaching world bench mark and which are the lowest of any Alcoa smelter
- Maintaining and protecting the rare species of plants that exist in the area
- Developing Portland Aluminium as a 'Smelter in the Park' with specific areas for the community to use for relaxation; for learning and research such as educational walks and bird hides; for wildlife habitat and for the smelting and manufacture of aluminium
- Reducing general waste materials to landfill from in excess of 1000 cubic metres per month in 1989 to less than two cubic metres in 2001
- Conducting regular community consultation meetings for the general community and for particular interest groups on specific topics
- Conducting regular tours through the smelter in association with the local tourist bureau
- Assisting in establishing and protecting the only mainland gannet colony in Australia
- Assisting in the protection and control of the numerous forms of wild life that enjoy the tranquillity of the Smelter in the Park areas
- Promoting the involvement of employees to assist in community activities
- Providing financial assistance to selected community organisations, projects and causes
- Liaising with the media on smelter activities that may impact on the local community

To fully appreciate many of the items in the above list would require considerable detail and is well beyond the scope or intention of this paper. The items are included to provide an awareness of practices that illustrate Portland Aluminium's commitment to its responsibilities for the environment and the community.

ALUMINIUM PRODUCTION

Aluminium is produced when an electric current is passed through an electrolytic cell or 'pot' which contains aluminium oxide (alumina) dissolved in molten sodium aluminium fluoride (cryolite) at 960⁰C. The pot is lined with a layer of carbon (cathode) and refractory bricks which isolates the carbon from the steel shell of the pot. Over the life of a pot (three to eight years) the linings absorb materials from the molten electrolyte. When a pot fails, usually due to cracking, erosion or deterioration of the purity of the aluminium being produced, the pot is taken out of service for repair and the remaining carbon and refractory linings are removed. They are known as Spent Pot Lining (SPL).

SPENT POT LINING

Spent Pot Lining is a waste product from the smelting of aluminium. SPL is considered to be a hazardous waste in various countries because it contains significant quantities of absorbed fluorides along with traces of cyanide. An increasing number of countries are banning the traditional method of landfill disposal of SPL. Approximately 20 tonne of SPL is generated for every 1000 tonne of aluminium produced. Hundreds of thousands of tonne of SPL are stored around the world awaiting a suitable means for its disposal. Disposal of SPL is the largest environmental problem of the aluminium industry.

SPL contains materials that are valuable if recovered and used for specific purposes. The main components having potential value are carbon and fluorides. The difficulties in developing a practice to recycle materials contained within SPL lie in the physical characteristics of SPL; the corrosive and toxic nature of the environment and products which occur within the treatment process; and the end products of that process.

Alcoa's Priorities re Generation and Treatment Processes for SPL

Alcoa has established a priority of actions relating to the generation and disposal of SPL. These are:

- Minimise generation of SPL per tonne of aluminium produced
 - ⑨ increase pot life through improved construction and pot operating practices.
 - ⑨ build new potlines with large sized pots

- Reuse components of SPL
 - Ⓣ in the aluminium smelting process
 - Ⓣ in other processes – industrial ecology
- Recover valuable resources
 - Ⓣ fluorides
 - Ⓣ carbon
- Treatment processes
 - Ⓣ eliminate hazardous conditions
 - Ⓣ ensure safe operating conditions
 - Ⓣ minimise waste output materials
- Disposal
 - Ⓣ minimum long term liabilities
 - Ⓣ effective end uses
 - Ⓣ landfill as a last resort.

SPL - SOCIAL AND ENVIRONMENTAL RESPONSIBILITIES

A specific example of Portland Aluminium accepting its social and environmental responsibilities relates to its treatment and disposal of SPL.

In 1989 Portland Aluminium committed itself to determine or develop the best process available for the treatment and disposal of SPL. This decision clearly indicated that Portland Aluminium was not prepared to construct buildings to store the ongoing generation of SPL material with the hope that some other organisation would develop an acceptable SPL treatment process.

Portland Aluminium's commitment to its social and environmental responsibilities was further illustrated in 1992-1994 when A\$2 000 000 was spent on trials in Australia and overseas in evaluating potential processes for treating SPL. Further confirmation of its commitment was the approval of up to A\$26 400 000 at the end of 1995 for the establishment of an R & D processing facility to treat SPL at Portland, Victoria, Australia.

The outcome of the expenditure of these funds was the development of 'The Alcoa Portland SPL Process'. This is a unique process that has involved high levels of innovation and technical risk. The following patents have been approved or filed for various components of the process.

- International Patent Application WO 94/22604, 6 April 1993: "Combustion of SPL via Top Submerged Lance Smelting."
- Provisional Patent Application Number PR 5194 "Process for the Production of Aluminium Fluoride"

PROCESS TECHNOLOGY INVESTIGATIONS AND DEVELOPMENT

In 1989 at the direction of Portland Aluminium's then plant manager, David Judd, extensive investigations were undertaken by Portland Aluminium employees in a world wide survey to evaluate past, present and potential processes for treating and disposing of SPL. At the time of the survey almost all of the fifteen processes examined were no longer operative, however a small number were selected for further study.

Pyrometallurgical Trials

After the expenditure of more than A\$2 000 000 during 1992-1994 on trials of these processes one process was considered worthy of more extensive development. The selected process utilised an Ausmelt furnace incorporating their Top Submerged Lance (TSL) technology. The pyrometallurgical process burnt the carbon material in the SPL and melted the SPL refractory components to form a slag product as reported by Jeppe, Matusiewicz and Goldin (1996). The furnace offgas contained high levels of the toxic gases hydrogen fluoride and sodium fluoride in addition to the normal gaseous products of combustion of carbon materials.

Aluminium Fluoride Trials

In 1995 the Portland SPL team, using Australia's Commonwealth Scientific Industrial Research Organisation (CSIRO), trialed synthetically produced hydrogen fluoride gas and smelting grade alumina to successfully produce aluminium fluoride. It was anticipated from this work that a grade of aluminium fluoride could be produced from the processing of SPL.

and used in the aluminium smelting process as a replacement for purchased commercial grade aluminium fluoride.

In December 1995 Portland Aluminium and Alcoa approved up to A\$26 400 000 for the construction of a facility to be built at the Portland Aluminium smelter site to treat SPL and to recover its valuable fluorides as aluminium fluoride. The project incorporated into its design the knowledge gained from the survey of organisations who had tried to process SPL, the results of the trials at Ausmelt and CSIRO and the information gained from Alcoa's aluminium fluoride manufacturing operation at Point Comfort in the USA.

OBJECTIVES OF 'THE SPL TREATMENT AND FLUORIDE RECYCLING PROJECT'

Prime Objective

The prime objective was to develop a treatment process for SPL that would destroy its hazardous condition, recover and recycle its fluoride content and dispose of the generated slag in an EPA approved method.

Specific Objectives

The specific objectives were:

- To destroy the cyanide component of the SPL
- To effectively use the carbon component of the SPL
- To recycle the sodium fluoride within the process
- To recover the fluoride components as aluminium fluoride suitable for re-use in the aluminium smelting process
- For the slag output product not to be harmful to the environment or human health
- For the slag output product not to be disposed of by landfill
- For the process to be economically viable

THE ALCOA PORTLAND SPL PROCESS

The flowsheet for the current plant operation is depicted in Figure 1. Three distinct areas exist. These are:

1. Pyrometallurgical process with related feed preparation and slag granulation
2. Offgas cooling, particulate removal and recycling
3. Production of aluminium fluoride and final scrubbing of the outlet gas

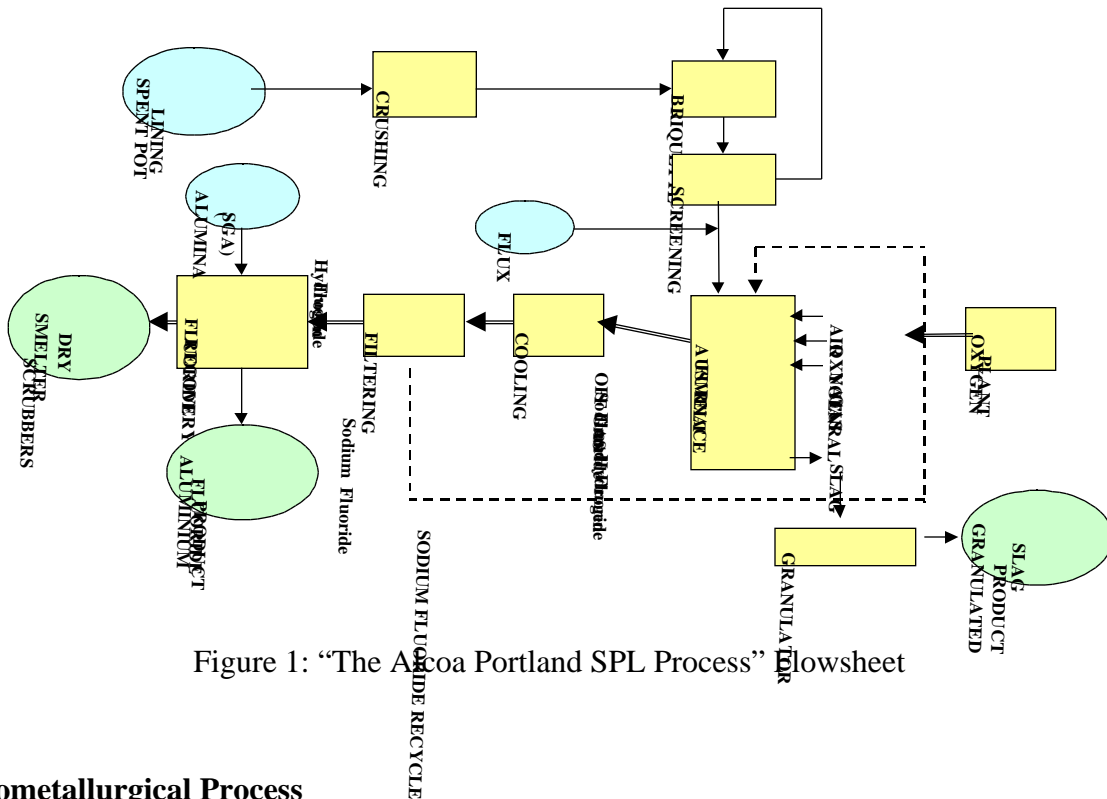


Figure 1: “The Alcoa Portland SPL Process” flowsheet

Pyrometallurgical Process

The Ausmelt TSL furnace (see Figure 2) can process feed materials up to 50 mm in size but is not suitable for processing small feed particle sizes. SPL when it is broken down by crushing or grinding, results in both small and large particles. Consequently it was decided to reduce all of the SPL to a small size and to agglomerate the fine material in the form of a briquette using molasses as a binder.

The high operating temperatures of the pyrometallurgical process, 1150°C to 1250°C, destroy all cyanide and organic materials in the SPL feed material. The energy to sustain operations at these temperatures is primarily provided by the combustion of carbon in the SPL and is

therefore effectively utilised in the process. The pyrometallurgical process capably treats all of the pot components including ceramic tiles, silicon carbide and refractory bricks.

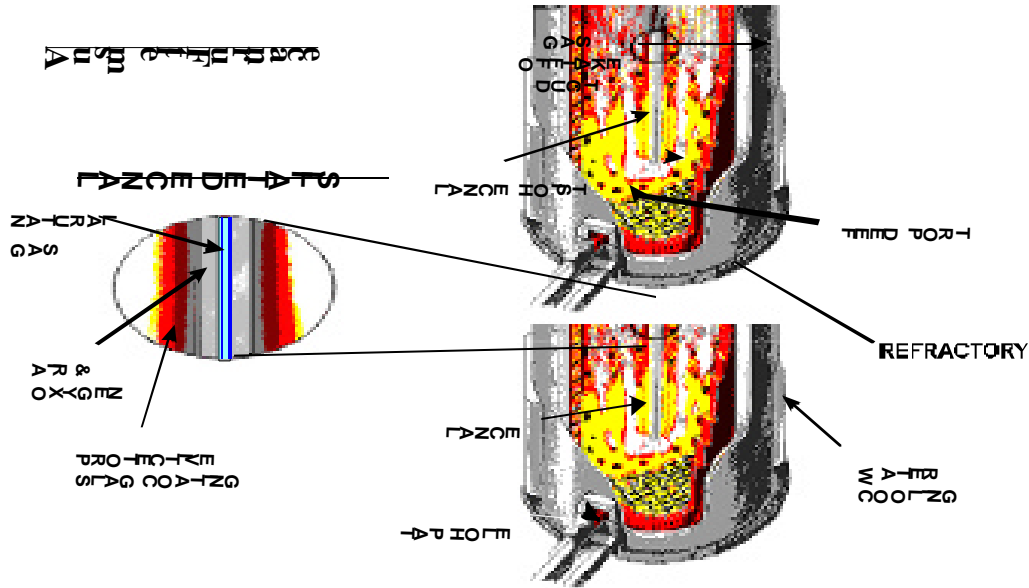


Figure 2: Schematic of Ausmelt Furnace

Refractories

Another significant challenge was to find refractory materials for the lining of the furnace that would withstand the high operating temperatures and the extremely aggressive slag and gaseous environment in the furnace. The presence of high sodium and fluoride levels in the slag plus a high level of hydrogen fluoride gas in an oxidising furnace atmosphere created unique and challenging conditions to all refractory suppliers.

Refractory life was initially only a few weeks. However through a series of experiments using thermocouples to determine the most suitable temperature profile across different refractory bricks and changes to operating practices the life between furnace relines, as at June 2002, has been extended to beyond sixteen months and was still performing satisfactorily.

Slag Flux

A flux material, (a waste slag product from an electric furnace steel manufacturing operation), containing high lime, iron and silica contents, is added to the furnace to assist in both the liquid mass transfer reaction sequences and in obtaining a liquid slag bath as illustrated by Floyd and Johnson (1999). The use of this waste product in the SPL treatment process is a good example of industrial ecology where waste from one industry is used or disposed in another industry.

Slag Leachability

An objective of the SPL treatment process was for the output slag product not to be harmful to the environment or to human health. Portland Aluminium and the Victorian EPA worked together to determine criteria for the slag that would not only achieve this objective but also would be economic and practicable for the process and would enable the slag to be used for commercial applications.

As a consequence Portland Aluminium installed a slag granulation process in June 2001 and modified the chemical composition of the slag in an attempt to achieve lower leachability values. The changes to the slag chemical composition were the outcome of commissioned work performed by Sun et al (2000) at CSIRO to improve slag leachability. The combination of these modifications has resulted in a granulated vitreous slag exhibiting significantly increased resistance to leachability. The leachability values of the slag now being attained are acceptable to the Victorian EPA to allow the slag to be used for unrestricted purposes.

Off-gas Cooling

The furnace off-gas contains high levels of the toxic gases hydrogen fluoride and sodium fluoride in addition to the normal gaseous products of combustion of carbon materials. To ensure the protection of the operators from the toxic gases the whole process is under negative pressure to prevent any gas leaks into the operator's working environment.

The cooling of the off-gases was an area where serious problems of blockages of off-gas ducts had been experienced by other organisations when treating SPL, and had resulted in the eventual failure of several processes. The blockages resulted from the accumulation of sticky

deposits of sodium fluoride during cooling at temperatures of approximately 800⁰C. To overcome this challenging problem a unique gas cooling process was designed and developed by the SPL team. The design has proven successful and has avoided blockages of the off-gas ducts. During further cooling the sodium fluoride gas transforms into very fine particulate that is removed from the system per medium of normal baghouse filters.

Recycling of Sodium Fluoride

For the overall SPL treatment process to be successful it was critical that the sodium fluoride was recycled to the furnace to produce hydrogen fluoride and for the sodium to be retained in the slag. Unless the recycling of sodium fluoride was achieved the limited uses available for this toxic and hazardous material would result in its unacceptable accumulation and the eventual failure of the SPL treatment process. Several problems had to be overcome to enable the safe and effective recycling to be achieved and the solutions to these problems are now part of the Intellectual Property of the process.

Production of Aluminium Fluoride

The formation of aluminium fluoride from the processing of SPL and the reuse of this material in the aluminium smelting process was a very significant challenge for the SPL team.

Development work was undertaken with CSIRO on a small scale experimental process to determine if it was possible to convert low concentration synthetically produced hydrogen fluoride gas and smelting grade alumina to aluminium fluoride. The results of the tests indicated aluminium fluoride had been formed and this was confirmed in limited trials using gases produced from processing SPL.

Reactor Design and Operation

Figure 3 shows the schematic of the reactor operation. Hydrogen fluoride laden gases from the pyrometallurgical furnace and gas cooling and filtering processes are reheated and passed through the bottom fluidised bed of partially reacted smelting grade alumina. The gases, partially stripped of hydrogen fluoride, continue to pass through two further fluidised beds and interact with the alumina in a counter flow configuration. The reactor does not absorb all

the hydrogen fluoride gas and some residual amount is passed to the smelter's dry scrubbing reactors for final absorption before being released to the atmosphere.

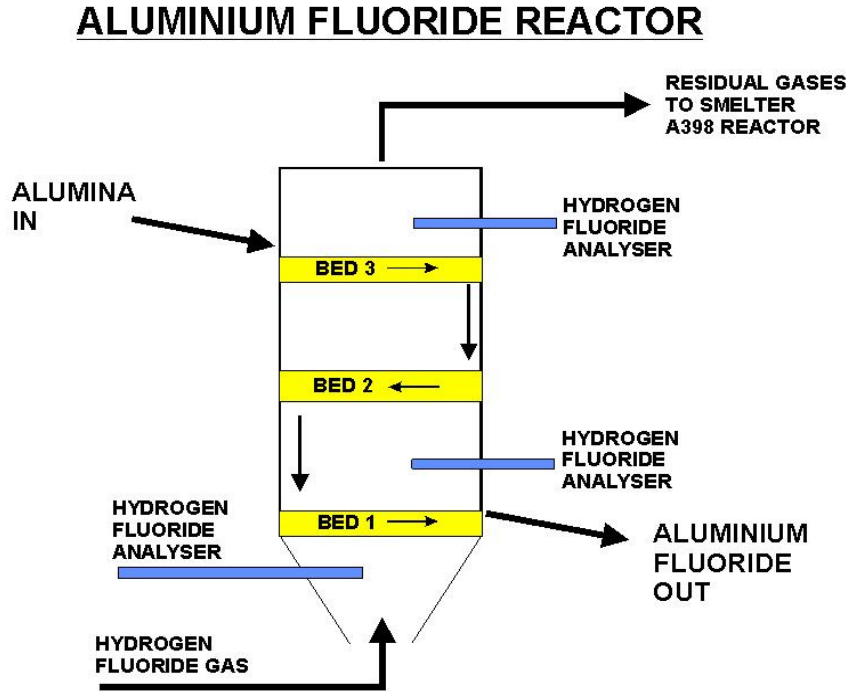


Figure 3: Reactor Flowsheet Showing Hydrogen Fluoride Gas and Alumina/Aluminium Fluoride Material Flow

RESULTS

Prime Objective

The prime objective, which was to develop a treatment process for SPL that would destroy its hazardous condition, recover and recycle its fluoride content and dispose of the generated slag in an EPA approved method, has been accomplished per the development of 'The Alcoa Portland SPL Process.'

Specific objectives :

The projects specific objectives have also been accomplished and are elaborated as follows.

To Destroy The Cyanide Component Of The SPL

Cyanide and any other organic materials present in the SPL are destroyed when exposed to the temperatures of 1150°C -1250°C that are experienced in the pyrometallurgical phase of the process. Chemical analysis of the slag and the SPL aluminium fluoride from the process has never detected the presence of any residual traces of cyanide.

To Effectively Use The Carbon Component Of The SPL

The heat required for the pyrometallurgical phase of the process is achieved from the combustion of natural gas and carbon in the SPL. Once heat is available from the combustion of the carbon the use of natural gas is significantly reduced. Consequently the value of the carbon in the SPL is effectively utilised by supplying heat to the process and reducing the amount of natural gas consumed.

To Recycle The Sodium Fluoride Within The Process

Several problems were encountered and progressively solved in order to achieve the recycling of the sodium fluoride particulate. Sodium fluoride is now readily removed from the baghouse and recycled into the furnace where it reacts with available hydrogen to form hydrogen fluoride that in turn is used to produce aluminium fluoride in the aluminium fluoride reactor. Sodium is eventually removed from the process by containment in the slag as various sodium compounds.

To Recover The Fluoride Components As Aluminium Fluoride Suitable For Reuse In The Aluminium Smelting Process

The successful generation of aluminium fluoride from the processing of SPL and the successful use of this material in the smelting of aluminium has been the significant difference between 'The Alcoa Bestland SPL Process' and any other process that treats or has

attempted to treat SPL. This outcome reduces the operating costs of the process by the savings through reduced purchases of imported aluminium fluoride and avoids using natural resources otherwise required for aluminium fluoride production.

SPL aluminium fluoride has a purity of 65-70% aluminium fluoride compared to 88–92% for commercial grade aluminium fluoride. Impurities in the SPL aluminium fluoride are minimal and are compared to the smelting grade alumina used in the process as shown in Table 1.

Table 1: Impurities in SPL Aluminium Fluoride and Smelting Grade Alumina (SGA)
(All values in ppm)

	Fe ₂ O ₃	Na ₂ O	SiO ₂	CaO	TiO ₂	Ga ₂ O ₃	K ₂ O
SGA	80	4000	120	420	40	95	5
SPL AlF ₃	79	3000	30	290	29	68	8

Two major trials using SPL aluminium fluoride in aluminium smelting operations have been performed. In June 1999, approximately 40 tonne of product was added to the pots in Alcoa’s Point Henry smelter in Geelong, Australian and a larger and longer trial (140 tonne and six weeks duration) was carried out in Portland Aluminium’s potrooms in July/August 2001. Harpley (1999) and (2001) indicated no significant differences were experienced in pot operation efficiency and metal purity from the usage of SPL aluminium fluoride compared to pots using commercial aluminium fluoride. See Fig. 4

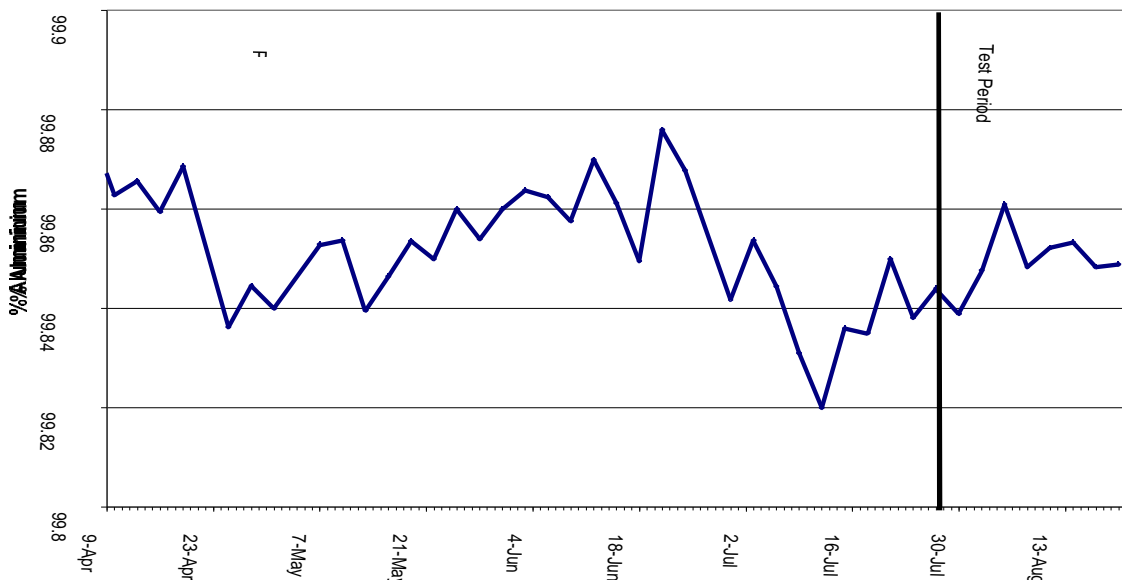


Figure 4: Aluminium Purity Before and During SPL Aluminium Fluoride Trial

For The Slag Output Product Not To Be Harmful To The Environment Or Human Health

The modified slag composition in combination with the granulation rapid quenching process, has resulted in increased resistance of the slag to leaching, due to the physical structure of the slag being highly amorphous and of a vitrified nature. The leachability values now being achieved for the granulated vitrified slag meet the Victorian EPA criteria for the unrestricted use of the granulated slag product.

Increased resistance of the slag to sodium leachability was evident by a reduction in leachate pH values for the granulated slag from 11 - 11.5 for standard slag chemistry to 9 – 9.5 with the modified slag chemistry. The increased resistance to fluoride leachability is demonstrated in Figure 5.

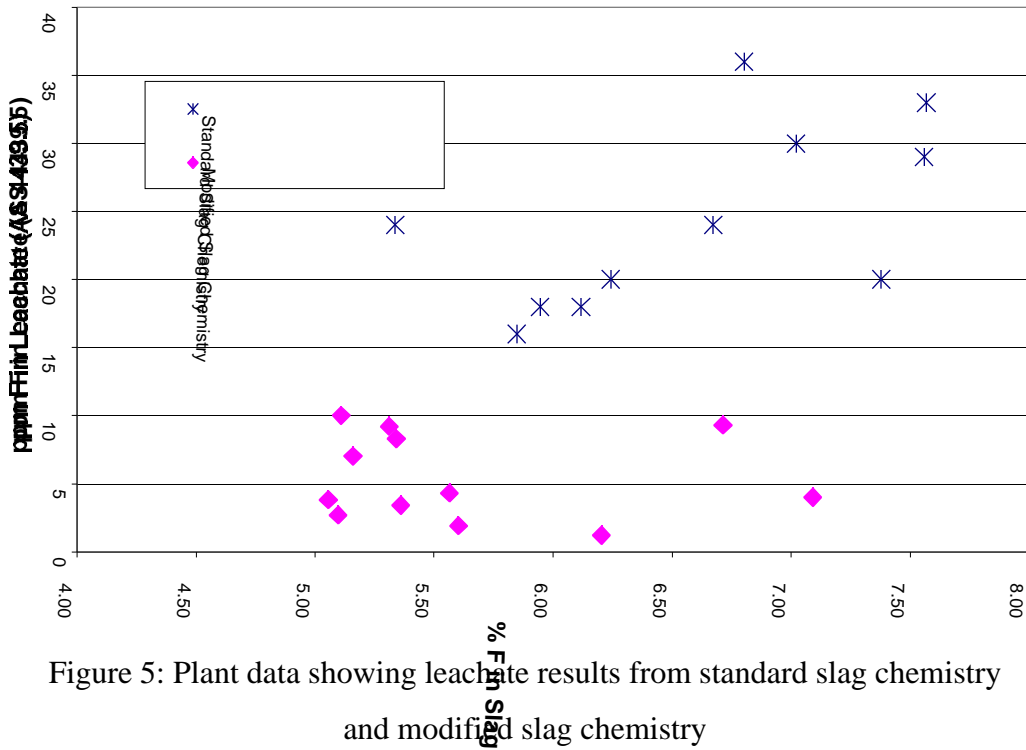


Figure 5: Plant data showing leachate results from standard slag chemistry and modified slag chemistry

For The Slag Output Product Not To Be Disposed Of By Landfill

Portland Aluminium has developed practices to achieve leachability values for the granulated vitreous slag product which conform to Victorian EPA criteria to permit it to be used for unrestricted purposes and consequently avoid it being disposed as landfill. The end uses of the

granulated slag are expected to be in road and pathway construction, replacement for specific types of sand and in cement and concrete manufacture.

For The Process to be Economically Viable

The operating costs of the SPL treatment process are lowered significantly by the savings achieved by using SPL aluminium fluoride instead of the expensive imported aluminium fluoride in the aluminium smelting process. 'The Alcoa Portland SPL Process' is very competitive compared to other known independent SPL treatment processes which usually do not achieve end products that are acceptable to EPA requirements re elimination of hazardous characteristics.

SUSTAINABLE DEVELOPMENT

'The Alcoa Portland SPL Process' encompasses sustainable development.

Environment Excellence

1. The process is a practical and economic solution to the largest environmental problem in the aluminium industry - namely effectively disposing of hazardous SPL waste.
2. The process produces aluminium fluoride from SPL and subsequently recycles fluorides within the aluminium smelting process, thereby conserving natural resources that would otherwise be consumed in the production of the equivalent amount of commercial grade aluminium fluoride.
3. The process produces a granulated slag having Victorian EPA approval for unrestricted use. The end uses of the slag are expected to be as in road construction and as a substitute for coarse sand in concrete manufacture.
4. The process avoids the need to landfill SPL or any of the process output products.
5. The process consumes a waste product from the electric steel manufacturing industry.

Economic Success

The processing costs of 'The Alcoa Portland SPL Process' are reduced by the high value of the commercial aluminium fluoride that would normally have been purchased for the aluminium smelting process, but which is avoided by using the SPL aluminium fluoride generated in the SPL treatment process.

The overall processing cost of 'The Alcoa Portland SPL Process' is an acceptable cost increase for the manufacture of aluminium for an environmentally responsible organisation.

Social Responsibility

Portland Aluminium displayed social responsibility when it decided not to landfill its SPL and in the commitment it made in 1989 to determine or develop the best process to overcome the environmental problems of the SPL hazardous waste product.

This social responsibility was again evident in 1995 when the partners of Portland Aluminium approved up to A\$26 400 000 to construct an R & D processing facility to effectively treat SPL at the Portland Aluminium smelter site and not to construct buildings to store the continuing generation of SPL until some other organisation developed an effective SPL treatment process.

FUTURE OF 'THE ALCOA PORTLAND SPL PROCESS'

'The Alcoa Portland SPL Process' is believed to be the best available to treat SPL and to overcome the biggest environmental problem in the aluminium industry. The process, as at June 2002, is continuously being improved as it increases equipment reliability and productivity in transitioning from an R&D project to an integrated operating facility.

The process will be available for use by others under a licensing arrangement. The marketing of the process will be in conjunction with Ausmelt Ltd, the company who supplied the furnace and whose pilot plant was used in the initial pyrometallurgical trials.

ACKNOWLEDGMENTS

Countless hours of contribution have been expended by past and present Portland Aluminium staff and operators, Engineering and PLC Control support staff as well as external inputs by numerous companies and research groups. The efforts of numerous people have enabled “The Alcoa Portland SPL Process” to reach this current stage and these efforts will be continued to ensure that it will achieve its full potential. The authors thank all for their input.

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