Recycling possibilities of spent potlining from the aluminum industry

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Abstract

Spent potlining (SPL) from aluminum reduction cell cathodes presents a major environmental concern in the primary aluminum industry. After laboratory tests it has been found that leaching cyanide and fluoride compounds present a major problem of SPL disposal. On the basis of the laboratory investigations, the possibilities of material and energy utilization of SPL have been studied. It has been concluded that SPL refractory material can be utilized directly in red brick manufacturing. A pilot test of the energy utilization of 25 tonnes of SPL carbon waste mixed with green petrol coke in a cement kiln has been performed. Additionally, the energy utilization possibility of SPL carbon waste in a coal thermal power plant have been investigated.
Keywords: re-use, spent potlining (SPL), red bricks industry, cement industry, co-combustion in thermal power plant.

1 Introduction

Aluminum is produced by the electrochemical reduction of alumina dissolved in fused cryolite (Na_3AlF_6) at temperature of 950 °C. This process is called the Hall-Heroult process, named after its inventors. It is the only method applied nowadays for industrial primary aluminum production.

At the end of the electrolysis cell (Figure 1) lifetime every 5 to 8 years it has to be shut down. Apart from the anodes, the bath, the metal and the bars, the material left is the cathode and is composed of:

- 55 % carbon cathode (referred also as "first cut"),
- 45 % refractory material (termed also as "second cut").

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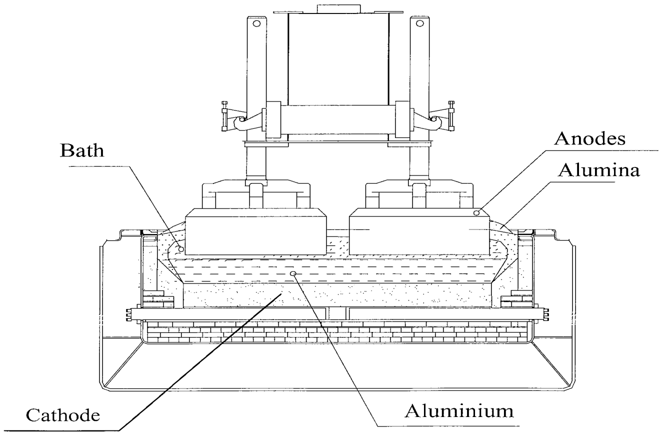

Figure 1: Schematic presentation of electrolysis cell.

Small smelters with little amount of SPL are trying to establish a co-operation with other companies for the possible utilisation of SPL materials. The bigger smelters are developing own disposal techniques in an effort to find a solution for this waste. Most of SPL is presently stored on site or deposited on secure landfill.

Some smelters separate the first cut from the second cut depending on the solution considered for SPL treatment. The re-use of SPL in other industries is made much more attractive if various SPL fractions are carefully sorted out.

Literature data (Berg [9]) for modern pot line indicates the total SPL is from 20 to 30 kg/t of produced aluminum. The total SPL generation in the world is estimated to be around 800,000 tones in the year 2003 calculated from expected total primary aluminum production of 28 million tons. During recent years the total amount of SPL per year has been decreasing, despite increased aluminum production. The reason for this is the choice of better cathode material, modern technology, and so on. Even in 1988, Brant Filho et al. [4] published that 30 to 45 kg of SPL per ton of aluminum had been generated.

Three major factors have contributed to finding a solution for SPL treatment:

1. SPL is classified as a hazardous waste,
2. Increasing waste-taxes,
3. Hazardous waste landfills requirements.

SPL material is mainly impregnated with soluble fluoride and cyanide compounds. Carbon is poorly wetted by a fluoride melt. The 14 % open porosity of cathode block materials is impervious to penetration. However carbon

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cathodes are fully impregnated with fluoride salt over sufficient time. One can simple say, that cyanide is formed by a reaction of Na, C (in the carbon part of cathode) and N_2 from the air.

All cyanides, and most fluoride compounds, are water soluble and leachate from SPL inventories may contaminate ground water or water run-offs. This represents important problem for the primary aluminum industry that must be solved.

2 Properties of SPL

2.1 SPL leachability

It is necessary to analyze waste material according to regulations before landfilling. Major concerns of controlled outside storage of potlinings has until recently focused mainly on the leaching of soluble cyanide and fluoride compounds. Leaching test results for both components, i.e. the first and the second cut SPL, are shown in Table 1 and 2.

Table 1: First cut SPL leaching test results and limit values.

Parameter	*Expressed as*	*Leacability result (mg/L)*	*Leachability limit values for sanitary landfill (mg/L)*	*Limit values for deposit on hazardous waste landfill (mg/L)*
cyanide-total	CN	163.42	0.5	20
cyanide-free	CN	121.63	0.1	10
fluoride	F	7.12	5	50

Table 2: Second cut SPL leaching test results and limit values.

Parameter	*Expressed as*	*Leaching test result (mg/L)*	*Leachability limit values for sanitary landfill (mg/L)*	*Limit values for deposit on hazardous waste landfill (mg/L)*
Fluoride	F	56.2	5	50

Leachability results in Tables 1 and 2 show that in both cases direct landfilling of the SPL material is not allowed, as the compliance with national limit values for sanitary landfills as well as for hazardous landfills cannot be reached without treatment.

2.2 SPL behavior under high temperature treatment

In the first step the total SPL behavior under high temperature treatment was investigated. Samples were taken from the first and second cut SPL of the pot at

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the end of its lifetime. The samples were crushed to a diameter below 1 mm. Then the samples were put in a furnace at different temperatures and kept for one hour. Finally, the samples were analyzed for fluoride and cyanide content (only in the first cut SPL).

Table 3: Cyanide content in first cut SPL after treatment at different temperature.

Temperature (°C)	*Cyanide content (%)*
20	0.033
100	0.030
110	0.028
120	0.027
130	0.023
137	0.019
147	0.017
157	0.016
167	0.011
177	0.008
181	0.008
184	0.005
186	0.005
188	<0.004
190	<0.004

At a temperature over 188 °C cyanide is apparently completely destroyed.

Table 4: Fluoride content in first and second cut of SPL after treatment at different treatment temperatures.

Temperature (°C)	*First cut SPL (%)*	*Second cut SPL (%)*
105	7.16	2.3
600	6.53	1.9
800	0.8	0.08
1000	0.17	-
1200	0.07	-

Table 5: Fluoride leaching test result after heat treatment at 1200 °C.

Samples	*Parameter*	*Expressed as*	*Leachability result(mg/L)*
1	Fluoride	F	40.82
2	Fluoride	F	44.3
3	Fluoride	F	42.2
Average:	Fluoride	F	42.5

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As shown in Table 4, the fluoride content in first cut SPL was significantly reduced by thermal treatment. At 105 °C the fluoride content was 100 times higher than at 1200 °C. After one hour temperature treatment at 1200 °C, the fluoride leachability in the ash (table 5) was consequently analyzed.

It is shown that even small amounts of fluorine in ash left after heat treatment (i.e. about 0.007%) present an environmental problem (with average fluorine leachability of 42.5 mg/L, see Tables 4 and 5). Hence it is necessary to stabilize fluoride in the ash before landfilling.

3 Re-use of second cut SPL in red brick manufacturing

In cooperation with a red brick company it was found a solution for the re-use of the second cut SPL (cathode waste bricks). The company already has a problem with fluorine content in clay (0.007 %), which is used as a raw material. Without flue gas cleaning system installed, the fluoride emission values are in the range from 19 to 22 mg/m^3. The current legislation limit for HF emission in the red bricks industry is 5 mg/m^3.

After homogenization of raw material and brick forming, the red bricks are backed in the temperature range from 800 to 850 °C, using natural gas for heating. Resulting flue gases from brick backing are led into the fluorine absorber. The absorber raw material is solid limestone ($CaCO_3$).

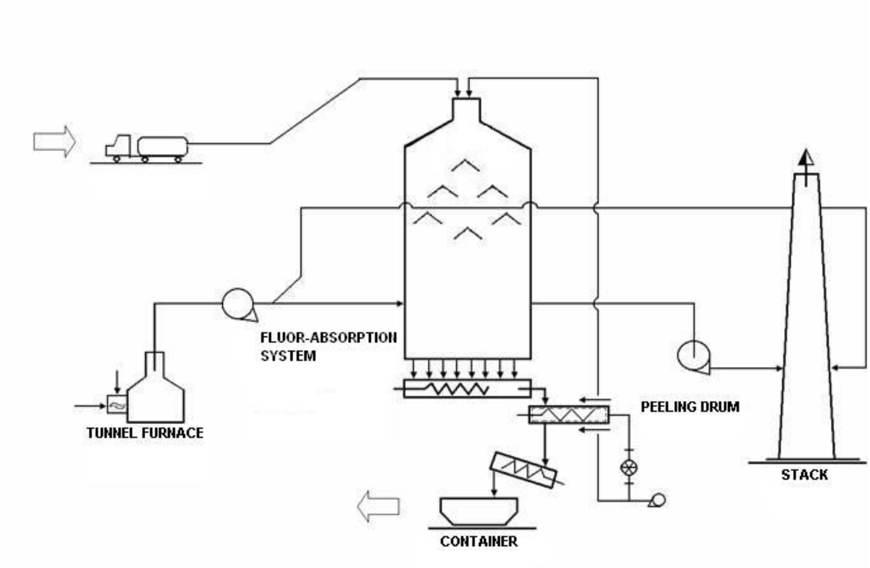

Figure 2: Flue gas cleaning system used in red bricks industry.

The chemical reaction, which takes place at the absorber, is defied as:

$$CaCO_3 + 2HF \rightarrow CaF_2 + H_2O + CO_2$$

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CaF_2 formed during the reaction is removed from the spent adsorber in the peeling drum. The peeled CaF_2 phase is used in concrete brick production. Thereby fluoride is converted into a very low water soluble phase of CaF_2 (lechability < 16 mg/l) and than further stabilized in concrete products.

For addition of second cut SPL in red brick manufacturing, the following factors have been investigated:

- influence on the red bricks properties (product quality),
- influence on fluoride emission in the air (environmental impact).

As a result, the following conclusions can be summarized:

- the properties of red bricks did not change by adding 5 % of second cut SPL to clay,
- fluoride emission to the air did increase, but still was below the national environmental legislation limit for HF emission, see Table 6.

Table 6: Comparison of measured HF emissions after flue gas cleaning, using only clay for red bricks production and clay with 5 % second cut SPL additives.

Base	*HF emission (mg/m^3)*
clay	1.2
clay with 5 % second cut	3.8

The limestone flow through absorber (consumption of $CaCO_3$) was not increased during the reported measurements; there were still enough reserve left. The upper limit for the addition of second cut SPL for re-use in red bricks manufacturing was found to be 5%.

Brant Filho et al. [4] reported pilot test, which was conducted in the red brick manufacturing. A process was developed for the utilization of total SPL in this industry. The bricks quality is said to be improved, and the use of first cut in SPL allowed up to 90% reduction in fuel (wood) consumption, applying a batch type backing furnace. Reported cyanide and fluoride emissions were below the limited level.

4 Re-use of first cut SPL

SPL composition depends on various factors, for instance the lining design, the temperature of metal, the bath impregnation, the lining materials, the cell age, the type of failure and the bath composition. The composition of first cut SPL used in this study is presented in Table 7. Data given are only examples of first cut SPL composition and cannot claim to be representative for the primary aluminum industry as such.

First cut SPL can mainly be utilized in the following two branches of industry:

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- clinker production (cement industry) and
- thermal power plants.

In both cases, first cut SPL is used as alternative fuel to replace a portion of the primary energy source.

Table 7: Composition of first cut SPL, used in this study.

Parameter	Unit	Standard method	Result
Humidity	%	Internal method	0.72
S	%	ISO 9055	0.17
F	%	ASTM 3761	7.16
Na	%	ASTM D 3682-87	9.42
Al	%	ASTM D 3682-87	5.23
Ca	%	ASTM D 3682-87	0.86
Si	%	ASTM D 3682-87	0.61
Cfix	%	ASTM 3172/73	56.13
Cyanide-total	%	ISO 6703-1	0.33
Cyanide-free	%	ISO 6703-2	0.03
Ash	%	ISO 8005	42.9
Caloric value	MJ/kg	ISO 1928	25.2

5 Re-use in cement works industry

Clinker is the base material in cement industry. Limestone (75-78%) with clay (marl) and some additives are used as the base material for clinker production. Clinker is calcinated at a bed the temperature 1500 °C. The cement plant investigated in this study uses natural gas and green petrol coke as fuel. The raw meal is preheated at a temperature of 850 °C in five-stage cyclone preheater system with flue gases from the rotary kiln. The base material (raw material) is basically a perfect absorber for acid flue gases. This makes it possible to burn a large spectrum of alternative fuels in the cement kiln.

Small additions of alkali (Na), alkaline earth (Ca) and fluorides increase rate of clinker forming reactions. As such, the rotary kiln can run at a lower temperature or at a higher rotation speed. Cyanide destruction was found to be completed at high temperature and fluoride emission was very low. Blanco et al [3] reported that cement properties were left almost unchanged by adding such a small portion (0.5%) of the first cut SPL to green petrol coke. Personnet [6] published that using (0,3 and 0,55 %) second cut SPL as additives to base material in the clinker burning process is possible.

6 Re-use in thermal power plants

Co-incineration of first cut SPL mixed with coal is possible in thermal power stations. When coal with a high amount of sulfur is used in thermal power stations, it is necessary to reduce SO_2 emission from the stack. The most

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economic way to do this is scrubbing of flue gas with milled limestone/water suspension (Figure 4). The primary reaction in desulphurization tower is:

$$CaCO_3 + SO_2 + 1/2\ O_2 \rightarrow CaSO_4 + CO_2$$

The reaction product is gypsum. Gypsum can be later used as a product or deposited at an inorganic type of industrial landfill. Besides the desulphurization reaction, defluorinezation reaction also takes place. The emission reduction rates are, in both cases, relatively high (92 – 94%) %. Study by Blanco et al. [3] concluded that it is possible to process first cut SPL in thermal power plants.

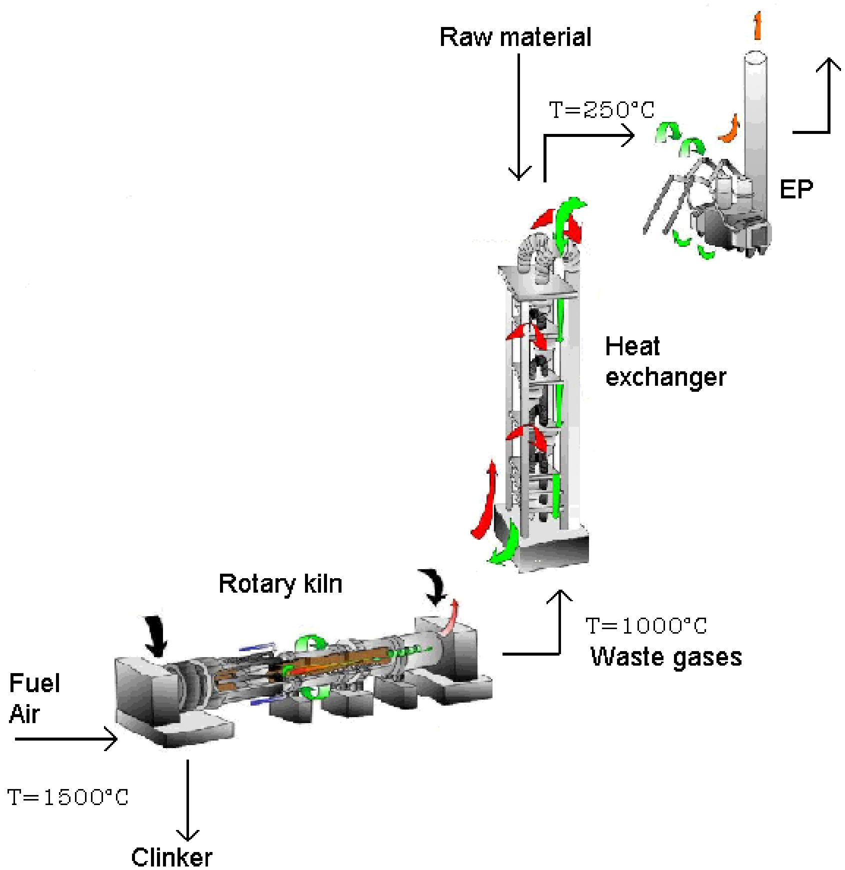

Figure 3: Clinker production process.

7 Comparison of SPL re-use in thermal power stations and cement industry

The fact is that favorable combustion conditions (i.e. 3T: time, temperature, turbulence) can be expected in a cement kiln. Due to fixation of acid gases like

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HF in the alkaline raw material and clinker, low HF emission can be expected. In the case of thermal power stations, according to national regulations, the HF emission is ten times higher as in the cement industry. In any case it is possible to utilize first cut SPL in both industries.

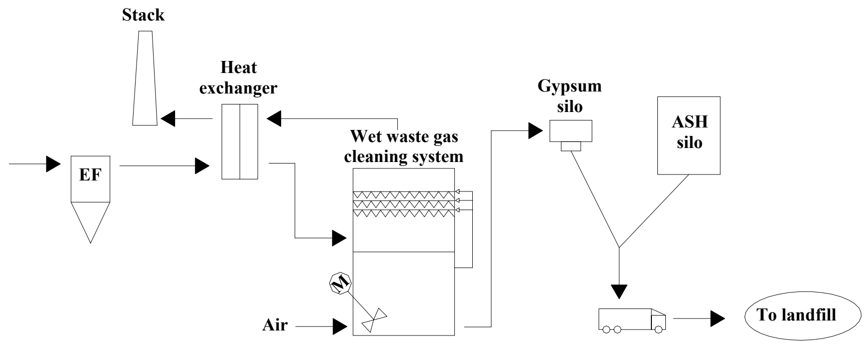

Figure 4: Desulphurization process in thermal power stations.

Table 8: Comparison of first cut SPL re-use in thermal power stations and cement industry.

	Thermal power station	*Cement industry*
Burning temperature (°C)	1,200 - 1,250	1,500
Cyanide decomposition (%)	100	100
Flue gas cleaning system	EP + wet scrubber with limestone suspension	dry absorption on raw meal (in heat exchanger cyclones
National fluoride emission limit (mg HF/m^3)	30	3
Co – combustion	mixing with coal	mixing with petrol coke
Mixed ration (%)	2	4
Expected consumption (t/h)	3	4
Expected emission value (mg HF/ m^3)	8-10	0.2-0.3
Ash	stabilised with gypsum for landfilling	no residue, fixed in clinker

The burn off is very slow because the first cut SPL does not contain volatile substances. In both cases is necessary grinding it below 1 mm. It is

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recommenced that first cut SPL is not to mixed with coal and/or green petrol coke, but used separately – i.e. to inject first cut SPL directly into the burning zone. Coal and green petrol coke contain water, which reacts with first cut SPL and form gases (CH_4, H_2, NH_3...).

8 Conclusions

In these studies, pilot test results are reported about the possibility of utilizing spent potlining (SPL) from primary aluminium industry in red brick production (for second cut SPL), thermal power stations and the cement industry (for first cut SPL). All three cases, no significant adverse impacts on the environment are expected, as long as the elaborated conditions for co – combustion are met. Cyanides and fluorides contained in SPL are destroyed or ab-/adsorbed during the utilization process.

More detailed studies as well as additional practical experience are necessary, before the utilization of SPL can be implemented at industrial scale. Furthermore, a feasibility study is necessary to evaluate the technical and economical aspect of utilization.

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