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ECONOMIC AND ENVIRONMENTAL ALTERNATIVE FOR DESTINATION OF SPENT POT LINING FROM PRIMARY ALUMINUM PRODUCTION

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Abstract

The residue from the demolition of electrolytic cells for the production of primary aluminum is the Spent Potlining (SPL). This material is classified as Class I (non-inert - traces of cyanide) waste. Among the possibilities of neutralizing the SPL there are the process at elevated temperatures with the formation of silicates and calcium compounds. The processes of secondary metallurgy of steel are characterized by high temperature and the slag is from the $CaO-Al_2O_3-SiO_2$ system saturated with CaO. Additionally, other fluidizing components used are found on the composition of SPL. In this work was investigated and evaluated the possible development and application of SPL as alternative in steelmaking.

Introduction

From the 50s, there was a significant expansion of the manufacturing sector that resulted in the early generation of solid and liquid waste from the various production processes without specific disposal and environmentally feasible recycling. The need for this allocation came from the 70s, when it was already registered significant environmental liabilities from the industries generally. Following Figure 1 below, we can see the global flow of aluminum (2011) and some of their waste.

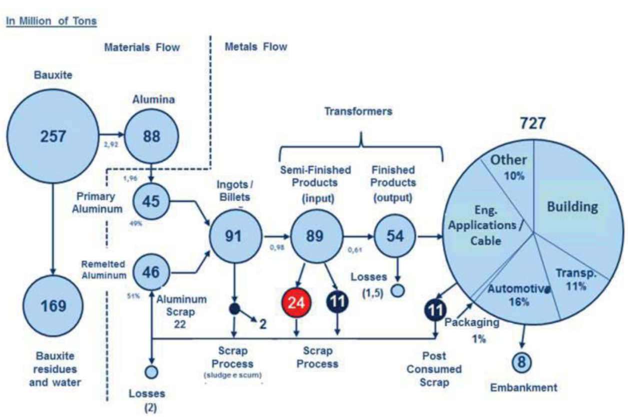

Figure 1: Aluminum production chain
Source: CRU 2012

Aluminum Production

The production process of aluminum begins with the extraction of bauxite (aluminum ore). The production of alumina (Al_2O_3) is through the Bayer process which consists in the digestion of bauxite in caustic soda, liquor purification, precipitation and calcination of aluminum hydrate.

The electrolytic reduction of aluminum is made in electrolytic cells, which are composed of a metallic casing internally coated with insulating materials, refractories, carbonaceous materials in the form of monolithic and carbon blocks that act as the cathode of the electrolytic cell. The anode is also formed of carbonaceous material and is consumed in the electrolytic process by reaction with oxygen.

The electrolytic bath comprises cryolite (Na_3AlF_6) (+ / -80%), aluminum fluoride (AlF_3) (+ / -7%), fluorite (CaF_2) (+ / -8%) and dissolved alumina (Al_2O_3) (+ / -5%).

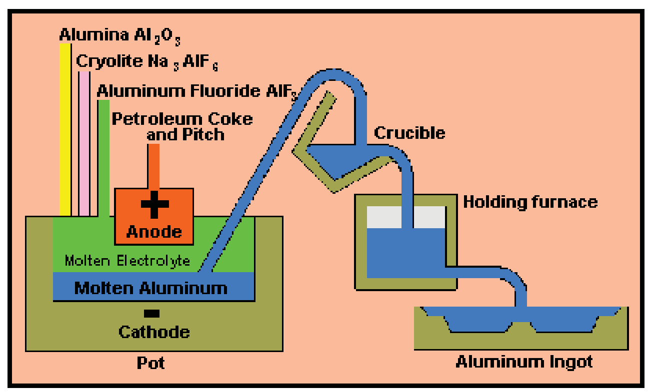

Figure 2: Flowchart of the process of primary aluminum

In theory in the electrolytic decomposition reaction of aluminum the cathode is not consumed in the process, but the cathode is submerged in liquid aluminum. However, the high temperatures involved (+ / -960 ° C), the presence of fluorides of sodium, aluminum and calcium, and other impurities, cause deterioration of the cathode and the need of periodic replacement. Votorantim Metais - CBA seeks to optimize and increase the life of pots, not only in order to minimize costs, but mainly to reduce the waste generation. Today the life of the pots is over 3,000 days.

Waste generation

Although there are several wastes generated in the aluminum industry, we focus in this work only on SPL.

The average of pot life is associated with the pot design and operating conditions. After the useful life the pot is shut down and all the material (refractory, cathode block and solidified bath) is removed, which is generating the SPL.

a) Physical-chemical characterization of SPL

The SPL is a heterogeneous material with refractory bricks and insulation plus carbonaceous material. It's impregnated by the fluorides of the electrolytic bath. The sodium from the electrolytic bath is one of the elements that mostly penetrate in the cathode blocks.

There are the formation of carbides and nitrides in the process that give rise of a small amount of cyanides.

The generation of SPL is about 30 to 50 kg/ton of primary aluminum.

Table 1: Chemical composition of SPL]
Source: Chemical Laboratory of VM-CBA

Amostra	F %	Na %	Mg %	Al %	Si %	P %	S %	K %	Ca %	Ti %	Fe %	W %	C %
01	19,09	23.33	0.15	33.56	14.18	0.05	0.36	0.85	4.39	0.66	3.25	0.15	9,69
02	20,03	22.97	0.20	33.52	13.60	0.04	0.35	0.73	4.30	0.63	3.49	0.14	9,83
03	18.34	23.19	0.16	33.51	14.59	0.04	0.38	0.80	4.63	0.62	6.60	0.16	10,1
Média	19.15	23.16	0.17	33.53	14.12	0.04	0.36	0.79	4.44	0.64	4.45	0.15	9,87

b) Potential applications of SPL

The main current application of SPL is the co-processing in cement clinker kilns (Cement), but also other applications have been studied. Examples are:

- Energy generation (carbon rich fraction)
- Mineral supplement in cement (clinker catalyst)
- Recovery of Fluoride
- Recovery graphite
- Additives for carbon cathodes
- Additives for carbon anodes
- Selective Metal Recovery
- Glass fibers (Rock Wool)
- Ceramic tiles
- Lime kilns

Proposal of this paper

Through research, analysis and testing we investigated the possibility of using the SPL in the steel industry, since its components are usual in this process especially in secondary refining. While this application is not new, we plan to tailor our operation with one or more Brazilian steel mills.

Additives for metal and slag:

- Fluxing agents (fluorides)
- Additive for electric furnace slag.
- Requirements: up to 30mm grain size and chemical composition homogeneous.

Application of SPL in Steelmaking

Carbon can act as reducing agents, generator of a reducing environment and fuel. In the steel desulfurization operations, it is beneficial by combining with oxygen whereby the carbon favors the formation of sulfides. If mixed with the covering slag from pans, distributors, ingot mold (conventional casting or continuous), it slows the melting of the slag thereby promoting thermal insulation. In the processes of injection it acts as a lubricant, facilitating the flowability through the lances. Unfortunately, it is undesirable in the case of low carbon steels.

Fluorides increase the fluidity of the slag and reduce its melting point. In the desulfurization process they increase the efficiency of lime, by disruption of the layer of CaS formed around the particles. They help the formation of liquid slag with low oxygen potential, favoring the protection against oxidation and improve the absorption of unwanted inclusions. But the downside is that the fluorides are potentially harmful for the refractory materials.

Alumina is a component of several synthetic slags in which they form calcium aluminates with low melting point and low activity of oxygen.

The Na2O acts as desulfurizing agent during melting and fluxing. It contributes to the formation of basic slag and improves fluidity but it can be aggressive for the refractory materials.

There are several other features that should be considered, but due to low concentrations they don't affect the conclusion regarding the feasibility of using SPL applications in the steel industry.

Methodology

The development of this work was trough to the following steps:

a) Characterization of SPL
b) Simulation of Slag Balance
c) Test in production line of steel

Characterization of SPL

It was analyzed two samples of SPL divided in two fractions as showing below:

Table 2: Characterization of SPL
Source: Magnesita Resarch Center

Calcined Base		
Oxide	Fraction	
	Bulk	Fine
PF	22,93	19,84
SiO2	38,6	27,26
TiO2	1,56	0,82
Al2O3	33,62	39,47
Cr2O3	0,04	0,01
Fe2O3	1,81	1,37
MnO	0,02	0
CaO	1,88	3,81
MgO	0,37	0,29
Na2O	21,24	26,25
K2O	0,73	0,64
P2O5	0,07	0,04
ZrO2	0,06	0,03
C total	22,16	19,91

Raw Base			
Oxide	Fraction		Average
	Bulk	Fine	
PF	22,93	19,84	21,39
SiO2	29,75	21,85	25,8
TiO2	1,2	0,66	0,93
Al2O3	25,91	31,64	28,78
Cr2O3	0,03	0,01	0,02
Fe2O3	1,4	1,1	1,25
MnO	0,02	0	0,01
CaO	1,45	3,06	2,25
MgO	0,28	0,23	0,26
Na2O	16,37	21,04	18,7
K2O	0,56	0,52	0,54
P2O5	0,05	0,03	0,04
ZrO2	0,05	0,03	0,04
C total	22,16	19,91	21,04

Simulation of slag balance for application on the steel production

The analysis was performed using the program SlagBal V3-5, considering manufacturing of a steel ASTM 1008 with the following additions during tapping (kg):

Table 3: Additives during metal tapping of Steel 1008

FeSi	FeSiMn	CaO	Aluminum	Fluorite
150	500	600	40	100

Furthermore, it was assumed in the simulation of the addition of 300 kg of slag from the furnace with the following composition (wt%)

Table 4: Chemical composition of slag

MgO	CaO	FeO	Al2O3	SiO2	MnO	Cr2O3	TiO2
7,4	28,6	34,9	5	16,1	5,3	1,5	1,1

Assuming:

- Yield of Si = 50%
- Internal diameter of ladle 2.7 m.
- Length of the arc in the ladle furnace is 100-mm
- Density of slag 2460 kg/m^3 for a $\Sigma R_2O_3 = 3\%$, is required approximately 1465-kg of mass of slag to protect the refractory from radiation of the electric

The idea is to take the slag in a region of the liquids line on the phase diagram, where it is just saturated with CaO and MgO at 1600 ° C. This point is about point O, as shown in Figure 4.

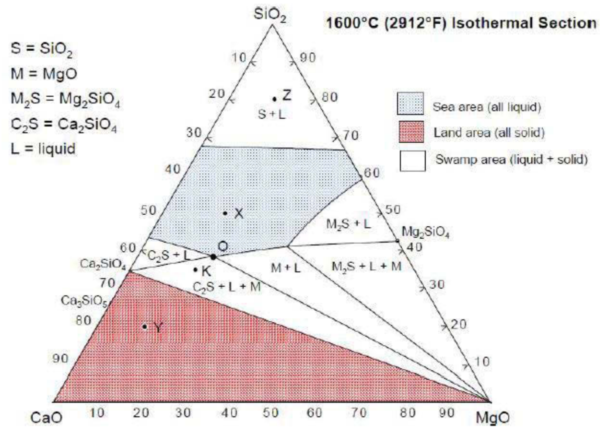

Figure 3: Ternary diagram, replacing Fluorite by SPL

For the purposes of mass balance was considered that the alkali (Na_2O & K_2O) from SPL has an influence similar to CaF_2. This mass balance was merely illustrative to show how much of fluorite can be replaced by SPL.

For the simulation it was considering the additions as shown the table 5:

Table 5: Additions of SPL and fluorite accord the simulation

Simulation of Slag Balance					
Run	Fluorite (kg)	SPL(kg)	CaO(kg)	FeSi(kg)	FeSiMg(kg)
1	50	60	500	200	900
2	50	60	500	200	900
3	50	60	500	200	900
4	50	60	500	200	900
5	100	60	500	200	900
6	0	100	500	150	900
7	0	100	500	150	900
8	0	100	500	150	900
9	0	100	500	150	900

The result of SlagBal simulation considering the production of steel ASTM 1008:

- The SPL is viable and should be used for steels of medium and high carbon, because it has all necessary features to assist the secondary refining, as fluxing and / or synthetic slag.
- In the case of low carbon steel is not recommended to use SPL due to the high content of carbon.

Test in production line of steel

Based on the simulation it was made 9 runs of steel whit the same addition of SPL and Fluorite during the metal tapping from the electric arc furnace (EAF) to ladle furnace (LF) on the Votorantim Siderurgia as known the steelmaker of the Votorantim Group.

Table 6: Additions of SPL and fluorite during the metal tapping

Additions during the run (AEF - LF)							
Run	Fluorite (kg)	SPL(kg)	CaO(kg)	FeSi(kg)	FeSiMg(kg)	Deficit of CaO(kg)	**Final Slag**
1	50	60	500	200	900	7	Fluid
2	50	60	500	200	900	117	Liquid
3	50	60	500	200	900	229	Liquid
4	50	60	500	200	900	157	Liquid
5	100	60	500	200	900	254	Liquid
6	0	100	500	150	900	81	Fluid
7	0	100	500	150	900	160	Fluid
8	0	100	500	150	900	92	Fluid
9	0	100	500	150	900	-15	Viscous

As noted in almost every run there was a deficit of CaO. The result of the fluidity of slag depends of the efficiency of Si as show figure 5:

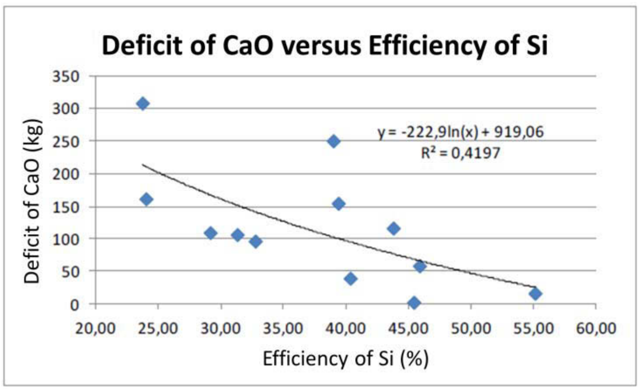

Figure 4: Efficiency of Si

The impact on the efficiency of Si is more related to the composition of the metallic charge (scrap) than the use of SPL.

The result of the test in the production line was evaluated according to the composition of slag input and output comparing to the specification of the process. The result of the runs is shown below:

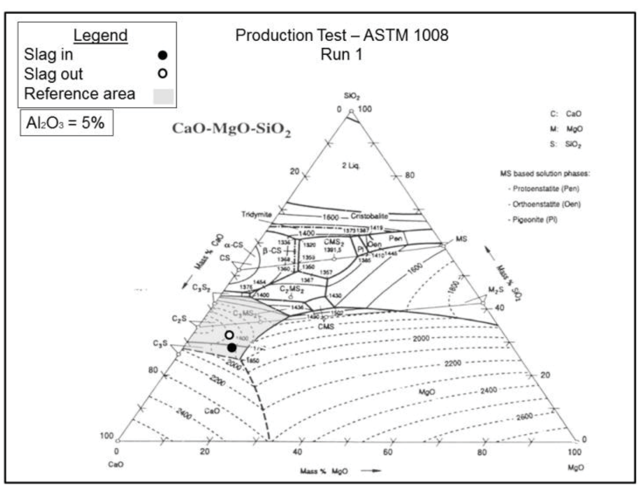

Figure 5: Test in production line – Run 1

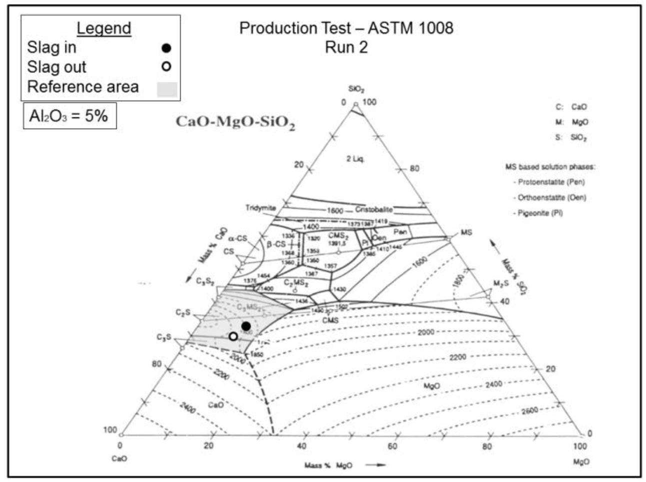

Figure 6: Test in production line – Run 2

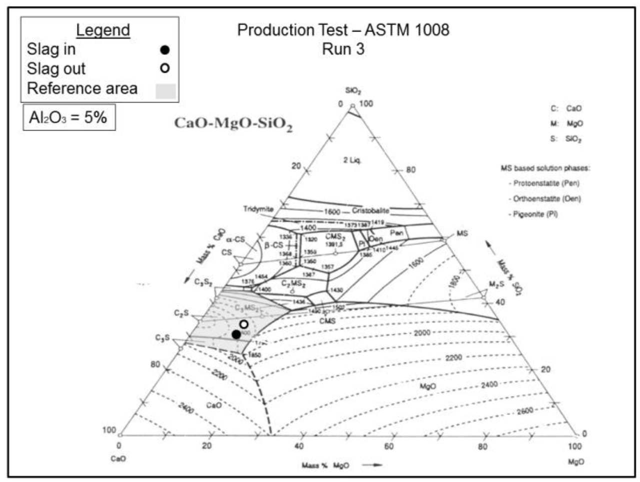

Figure 7: Test in production line – Run 3

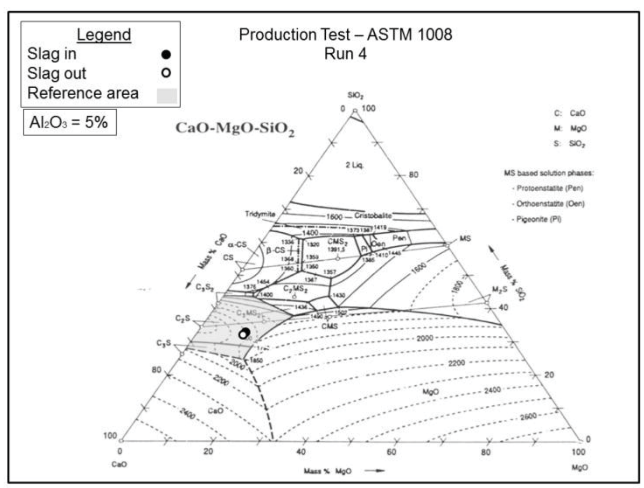

Figure 8: Test in production line – Run 4

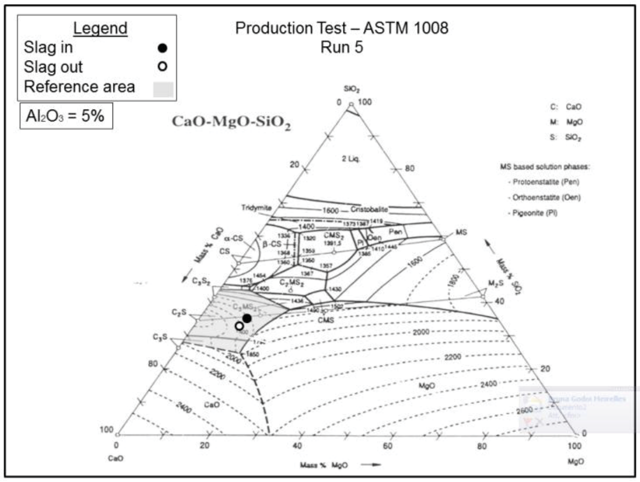

Figure 9: Test in production line – Run 5

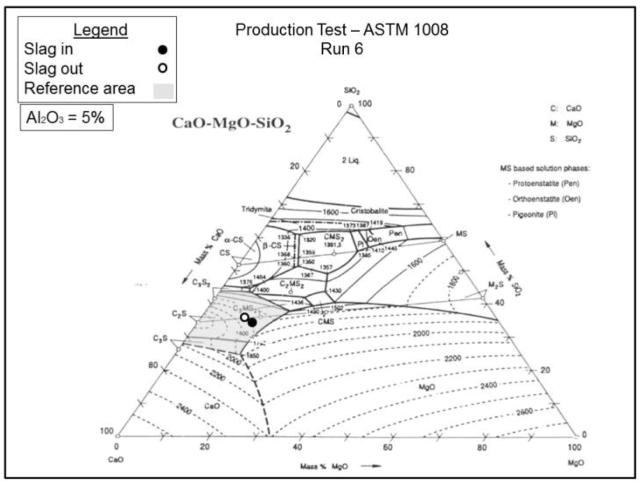

Figure 10: Test in production line – Run 6

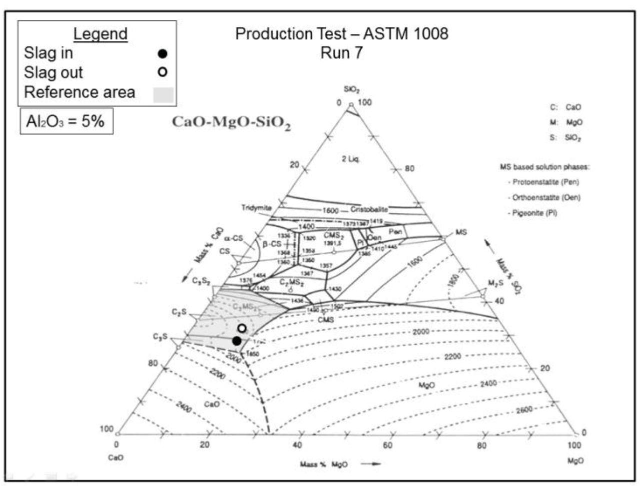

Figure 11: Test in production line – Run 7

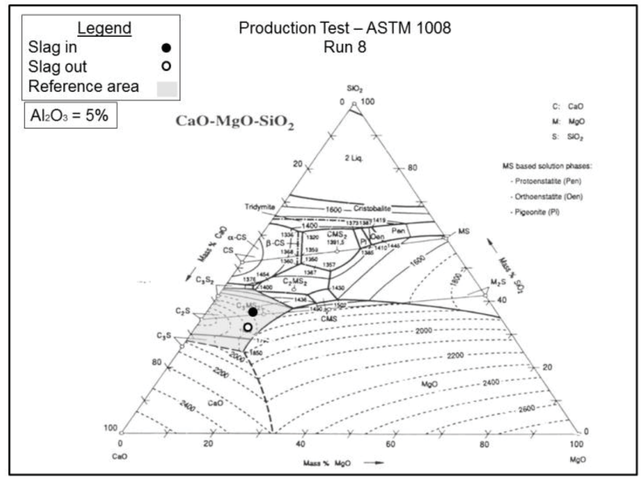

Figure 12: Test in production line – Run 8

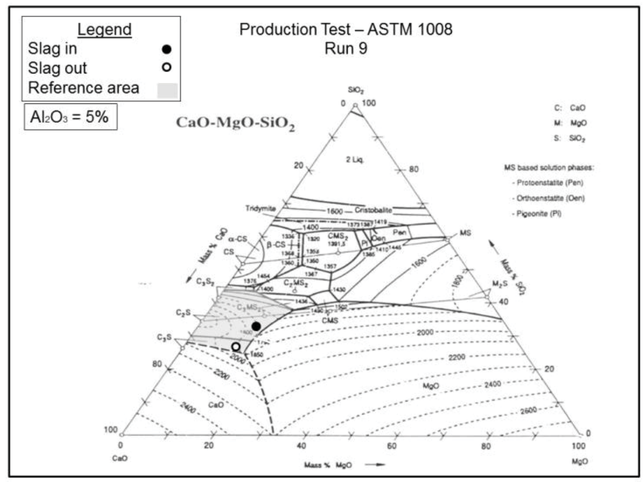

Figure 13: Test in production line – Run 9

We could reach the appropriate composition of the slag using different additions of SPL in all nine runs.

100 kg of SPL and 600 kg of CaO are enough to have a fluid slag, saturated CaO / MgO and with sufficient volume to cover the arc.

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These additions are valid only for this type of steel using 900 kg of FeSiMn, 120 to 200 kg of FeSi during metal tapping. For other types of steel with different additions would be to run a new model. The additions should be on the metal tapping from the EAF to LF.

Conclusion

It's possible to replace the fluorite by SPL as fluxing slag. The high cost of the fluorite turns the process of use of the SPL economically viable since the most companies have spent money to allocate this waste.

This result shows that it's possible use SPL in production of several types of steel by making the necessary adjustments.

Reference

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