

## USE OF SPENT POTLINING (SPL) IN FERRO SILICO MANGANESE SMELTING

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### Abstract

In this work an evaluation of the possibilities to employ Spent Potlining (SPL) as a component of the burden of a Submerged Arc Furnace (SAF) producing Ferro Silico Manganese Alloy is investigated.

On this subject, a characterization of the SPL's most probable components as well as their interaction with the existing species in the ferroalloy furnace were carried out. Additionally relevant features of the ferroalloy smelting were identified and characterized. Those figures were introduced in a thermo chemical program where the SAF operational conditions were simulated in order to check the technical feasibility of that use.

The simulation results showed that, on the technical point of view, the SPL carbonaceous fraction is a suitable component of the SAF burden, producing Ferro Silico Manganese alloys.

Although some of the figures generated by simulation were confirmed in several industrial exploratory tests, a more detailed test program is advisable.

### Introduction

The electrolytic cells employed in aluminum winning are lined with carbon that is in contact with the bath and metal and insulating material placed between the former and metallic shell. Through its operating life, the cathode lining changes chemically and physically, that leads to its expansion and deterioration. As a consequence a splitting process grows up and after a

period that goes from 2000 to 3000 days, the pot cathode lining fails and must be rebuilt. At this time, the old lining is dismantled. This material is called SPL (Spent Pot Lining) and is constituted of the starting lining material and the components absorbed during the operating pot life. Figure 1 shows the steps of the SPL formation [1]

SPL can be easily separated in two well defined fractions:

The carbon fraction is constituted of the old cathode blocks and non carbon fraction, constituted of old refractory and insulating bricks, ramming paste, electrolytic bath and a series of components formed by the interaction between those components and metal and air.

From a general point of view, the reductant is the chief cost item in carbothermic reduction process. Among these processes are the manganese alloys smelting. Ferro Silico Manganese smelting is an electrometallurgical carbothermic process. In such a process, besides its reducing characteristics, carbon is the main element responsible for the electrical characteristics of the burden.

Last, but not least, the ash content and composition have an influence on slag volume and characteristics and, depending on the nature of other components, on alloy quality and furnace operation.

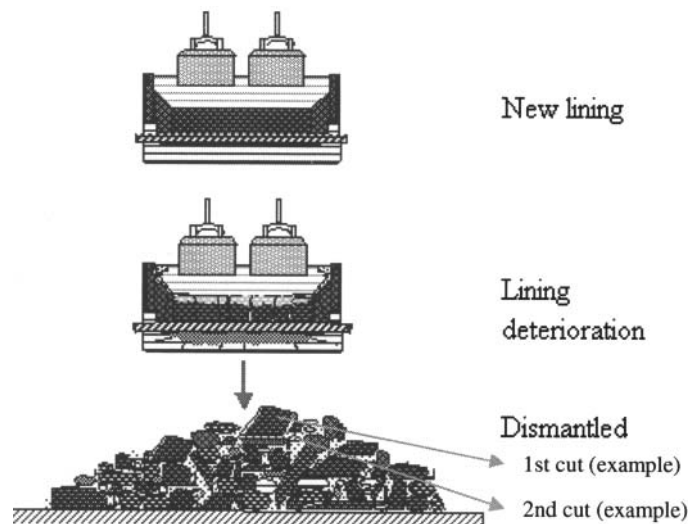


Figure 1 – SPL formation scheme [1]

In this paper the possibilities for employing the SPL's carbon fraction as a burden component on ferroalloys smelting is evaluated. Specifically, the selected ferroalloy is from Ferro Silico Manganese type.

In a first approach, aiming to check the technical feasibility of that alternative, the main physical and chemical characteristics of the SPL are established and the resultant data will be "introduced" in the Ferro Silico Manganese furnace burden and the furnace behavior with this new component was analyzed. Although this first evaluation is a theoretical approach, it indicates if there are constraints that would impair this application. The next step, industrial scale trials would be essential.

### Spent Pot Lining (SPL) Essentials [2]

The aluminum pot lining is constituted of a series of components, each with its own purpose.

Figure 2 shows the scheme of a typical lining. [5] As can be seen, the bottom lining is constituted of three kinds of non carbon materials and a fourth that are the carbon blocks.

Among the non carbon materials, the berth is an alumina layer, the refractory are silico-aluminous bricks and the insulating layer is made of low density and low thermal conductivity bricks.

Not characterized in the figure, the side lining is constituted of carbon bearing paste, silicon carbide and ceramic materials

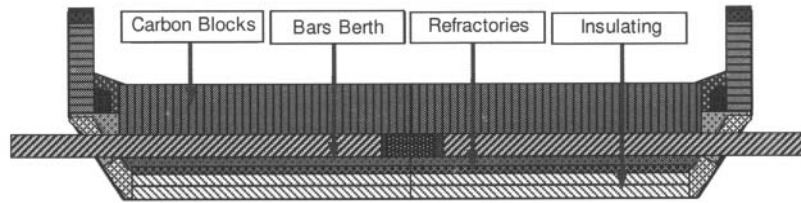


Figure 2 – Pot lining scheme (typical)

Carbon blocks, constituting the top layer of the bottom lining, are by far the most important component of this system. The carbon block assemblies form the cathode of the electrolytic system.

Carbon blocks must meet several requirements: among them are high electrical conductivity, low reactivity and high mechanical strength.

Depending on the type of the block, those properties can vary among a relatively ample range, in a new lining. However, during their operating life, the blocks absorb bath components and interact with it and the surrounding environment. Within this process, both the physical and chemical characteristics change. For the purpose of this paper, the properties to be considered are those existing at the end of the lining life.

### Chemical Characterization

SPL material comprises carbon and refractory materials, penetrated metal and bath components and minor amounts of aluminum nitride, aluminum carbide and cyanide salts. There is not an exact composition of SPL; it varies over a wide range, depending on several factors, such as lining design, pot age, etc.

The whole of SPL can be divided in two "cuts"; the first cut corresponds to the carbonaceous part (carbon blocks) and the part of the lining beneath the blocks assembly correspond to the second cut.

Table I shows typical composition of SPL, as well as those from the first and second cuts. According to what was mentioned before this is just a reference composition

Table I. SPL's typical components and concentrations			
Component	Total (100%)	First Cut (carbonaceous) (56%)	Second cut (non carbonaceous) (44%)
Carbon	33.1	54-64	18.2
Total Fluorides	15.7	6-20	4-10
Free Alumina	22.3	0-15	10-50
Total Aluminum	15.1	5-15	12.6
Total Sodium	14.2	5-12	12.0
Calcium	1.8	0.5-4.0	1-6
Quartz	2.7	0-6	10-50
P	0.3	0-650 g/t	0-300 g/t
Sulfur	0.1	0.1	0.1

As suggested in the third drawing of figure 1, the first cut is constituted of big pieces of high resistance carbonaceous materials, from the former cathodes blocks. The second cut is a mix of paste, refractory

and insulating material, whose properties are extremely variable, both geometrically, physically and chemically. Both cuts are impregnated with bath components and metal.

As will be seen later, the material that meets the most suitable properties, considering the burden characteristics of a Ferro Silico Manganese furnace, is the first cut, both from the chemical, physical and metallurgical point of view.

On the other hand, a greater part of the second cut is constituted of loose or powdery material that would seriously impair furnace operation. This suggests that only the carbonaceous fraction (first cut) can be considered for the proposed application.

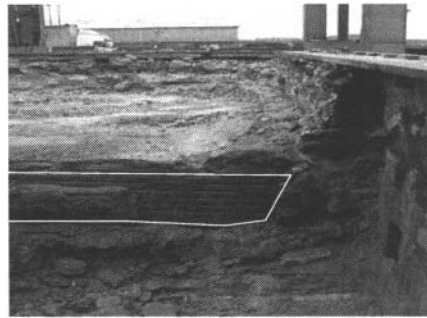


Figure 3. Section of the lining of an aluminum pot, during its dismantling (light line enhances carbon blocks)

In order to evaluate the metallurgical behavior the figures shown in Table I must be detailed, identifying the actual compounds present in the material, specifically in the first cut.

For that, the possible reactions between carbon lining an surrounding components, as well as their relative preferences must be known and analyzed.

Although the whole of the spent potlining are together from the pot cathode, fortunately the two cuts are quite different and can be easily separated each other.

The photo of Figure 3 shows pot being dismantled. As can be seen, there is a sharp difference between the carbon blocks (1<sup>st</sup> cut) and the other components (2<sup>nd</sup> cut)

The number of reaction is extensive; for the sake of simplicity this paper only considers the most relevant.

Figure 4 shows the evolution of the main compounds during the pot lifetime. For the purpose of the present work, the reference figures are those at the time of pot shutdown.

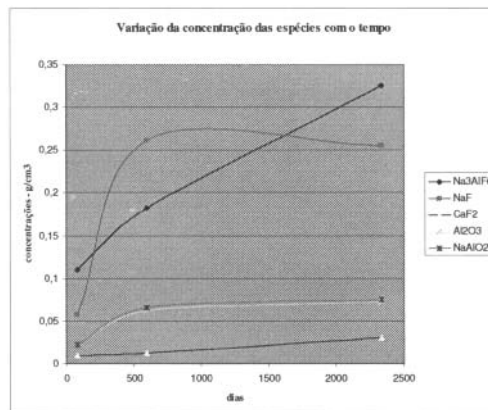


Figure 4. Variation of the main species concentration with time [2]

Besides these components there are the carbon and quartz. Both the former and the later are diluted during lining life. Based on these aspects, the SPL Carbonaceous fractions were calculated with the resultant values shown in the following list. Naturally, it must be pointed out that these figures can vary from plant to plant. Another remark is that the criolite and sodium aluminate were decomposed in its elementary compounds with the purpose of the metallurgical operation evaluation.

AlF <sub>3</sub>	7.18%	Na <sub>2</sub> O	1.22%
NaF	22.70%	SiO <sub>2</sub>	5.00%
CaF <sub>2</sub>	1.55%		

#### Electrical Properties

Electrical resistivity is an important parameter both in aluminum and in ferro silico manganese smelting. In the first instance, the resistivity must be as low as possible. For the ferroalloy smelting the operation is carried out in a submerged arc furnace; the high temperature zone depends on the electrode tip

SPL reference composition:

C	55.98%	Al <sub>2</sub> O <sub>3</sub>	6.37%
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position that depends on the voltage and burden resistance.

During its operating life, the aluminium smelting cathode block is submitted to two kinds of processes:

graphitization and impregnation. The first one improves the conductivity and the later increases the resistivity. Figure 5 shows this variation both in ambient and operating temperatures.

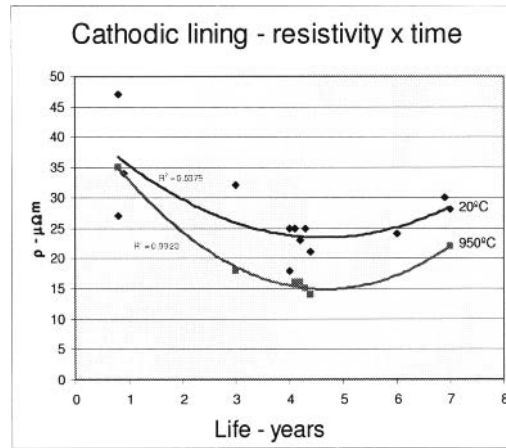
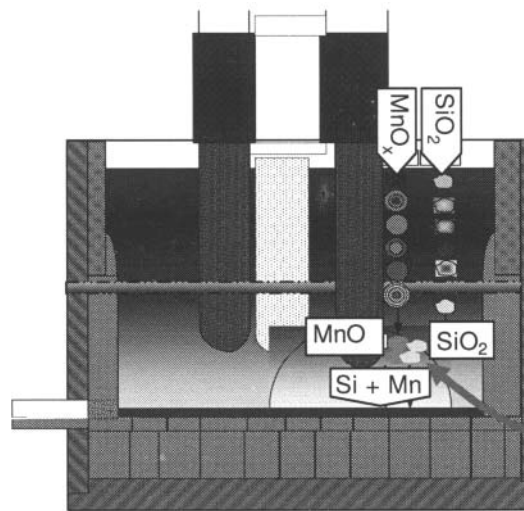


Figure 5. Cathode block – change of the resistivity during operating life [3]

The negative slope in the first section of the curves suggests that during initial cathode operation that graphitization prevails over impregnation of both species. The positive slope in the final section indicates that the block is already fully graphitized

and only impregnation occurs. Based on that it can be said that at the end of its useful life, the resistivity of a cathode block are nearly the same, doesn't matter if it was originally of amorphous carbon or fully graphitized types [3]



Reduction temperatures - selected oxides

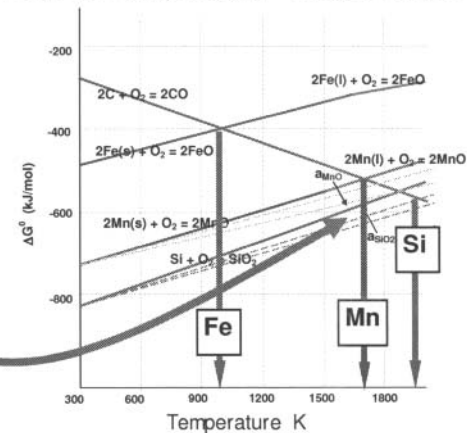


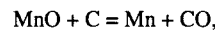
Figure 6. FeSiMn smelting scheme (easily reduced iron is not shown) and reduction temperatures

#### Ferro Silico Manganese (FeSiMn) Essentials[6]

Production of FeSiMn is carried out by the simultaneous reduction of manganese and silicon, by carbon, in submerged arc furnaces (SAF), as shown schematically in figure 6.

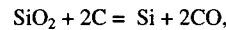
Burden is constituted by manganese ore, manganese bearing slag, quartz (or quartzite) carbon source and fluxing agents.

The manganese reduction temperature from its lower oxide, MnO:



depends on its activity in slag; the higher the concentration of free MnO, the lower the reduction temperature. On the contrary, the higher the concentration of MnSiO<sub>4</sub>, the higher its reduction temperature (fig 6).

Reduction of silicon from silica (SiO<sub>2</sub>):



requires higher temperatures, as shown in figure 6.

Therefore, in order to get a more intense reduction of Silicon, the Manganese reduction temperature must

be higher, that means higher concentrations of silica in the slag. On the other hand, the more silica in slag, the more viscous is it. As far as high viscosities impairing the mobility of reagents, inhibiting the reduction reactions, one can conclude that the higher the concentration of Silicon in FeSiMn alloy, the more difficult the process (indeed, there is a limit above it that the process is not feasible).

There are several ways to determine slags viscosities. This can be done experimentally or applying empirical expressions or diagrams. In this paper the hereafter expression [4] was adopted because it considers species encountered in SPL and so its influence can be evaluated. This is a theoretical approach that should be confirmed experimentally, but for the purpose of this work, it is considered acceptable.

$$\ln \mu = -12,0 + 0,0525(\%Al_2O_3) + 0,0881(\%SiO_2)^* - 0,0409(\%CaO)^* - 0,0421(\%Na_2O)^* - 0,0194(\%F)^* + 14941/T$$

where

$$(\%CaO)^* = (\%CaO) + (\%MgO) + (\%MnO) + (\%FeO) + (\%B_2O_3)$$

$$(\%SiO_2)^* = (\%SiO_2) + (\%P_2O_5) + (\%TiO_2) + (\%ZrO_2) + (\%Fe_2O_3)$$

$$(\%Na_2O)^* = (\%Na_2O) + (\%K_2O) + (\%Li_2O)$$

$$(\%F)^* = \Sigma(\% \text{ Fluorides})$$

Though not being necessarily precise, the qualitative influence of the components on slag viscosity is well posed.

### Process Evaluation

Based on the features of the FeSiMn smelting and on

Table II. FeSiMn smelting – Results of simulation – conventional procedure

Inputs	kg/ t alloy	Chemical composition			
		Alloy		Slag	
Manganese ore	1668	Si	22.31%	SiO <sub>2</sub>	41.61%
Mn rich slag	910	Fe	13.45%	Al <sub>2</sub> O <sub>3</sub>	23.20%
Quartz	334	Mn	63.55%	CaO	18.19%
Limestone	230	Al	0.00%	MnO	16.62%
Coke	369	C	0.70%	CaF <sub>2</sub>	0.00%
Petcoke	155	P	0.02%	NaF	0.00%
SPL	0				
Outputs	kg/ t alloy	Electrical Energy		Viscosity	
Alloy	1000	3762 kWh/t alloy		0.58	
Slag	929				

### Process Simulation [5]

In the reference process, without SPL, it was considered a conventional operation, using manganese ore and manganese rich slag (from HCFMn production), quartz and limestone. The reducing agent was a mix of metallurgical coke (70%) and petroleum coke (30%), which is a blend in manganese alloys smelting operations.

Table II shows the results of this simulation

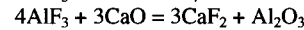
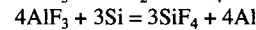
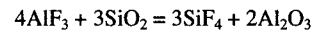
the SPL characteristics presented above, two simulations [5] of the SAF operation with and without SPL in the burden were carried out. The purpose is to evaluate by comparison, the technical feasibility of the former. All other components were the same in both cases.

The simulation was carried out by means of a thermochemical program previously developed for the evaluation of ferroalloys smelting procedures. Its validation was made by the comparison with actual operations [5,7].

### Side Reactions [3,7]

Before going on with the simulation, a thermodynamic analysis was made, aiming to identify the most probable reactions and the resultant compounds. The behavior of the oxides is well known and is the same for both alternatives. The Na<sub>2</sub>O behavior can be compared to that of K<sub>2</sub>O that is a very common component in manganese ores.

On the fluoride side, NaF and CaF<sub>2</sub> are quite stable and are incorporated in the slag. Aluminum fluoride (AlF<sub>3</sub>) may react with silica, silicon or lime, according to the following reactions



Considering the furnace temperature and the concentrations of the species, it was assumed that all AlF<sub>3</sub> would react with SiO<sub>2</sub>, forming volatile SiF<sub>4</sub> (first reaction)

The formation of CF<sub>4</sub> is not likely to occur.

In the simulation with SPL it was considered that it was introduced substituting petroleum coke. As far as carbon content of petcoke (>90%) is much greater than that of the first cut of SPL (~54%), the substitution on a weight by weight basis implies in the charging of additional metallurgical coke, to achieve the required carbon. The mass balance of carbon was completed by means of metallurgical coke in order to keep the burden resistivity constant. Table III shows the results of this simulation.

Table III. FeSiMn smelting – Results of simulation – procedure with SPL

Inputs	kg/ t alloy	Chemical composition			
		Alloy		Slag	
Manganese ore	1678	Si	22.31%	SiO <sub>2</sub>	39.30%
Mn rich slag	910	Fe	13.45%	Al <sub>2</sub> O <sub>3</sub>	23.61%
Quartz	334	Mn	63.57%	CaO	17.18%
Limestone	230	Al	0.00%	MnO	15.70%
Coke	428	C	0.66%	CaF <sub>2</sub>	0.25%
Petcoke	0	P	0.02%	NaF	3.60%
SPL	155				
Outputs	kg/ t alloy	Electrical Energy		Viscosity	
Alloy	1000	3793 kWh/t alloy		0.47	
Slag	984				

Comparing the results from the two tables it can be seen that all but the reducing agent, components proportions are practically the same in both cases. The slag weight is greater when SPL is employed due to its ash content being greater than that of petcoke; this also implies greater energy consumption. On the other hand the sodium and fluoride content of SPL lead to a lower slag viscosity, what enhances the reaction efficiency.

From the electrical point of view the burden must have suitable resistivity by assuring optimum positioning of electrode tips. For that it would be desirable that the SPL resistivity be similar to that of the substituted reducing agent. Figure 7 shows the change of the resistivity with temperature for charcoal, coke and SPL[2,3 and 6]

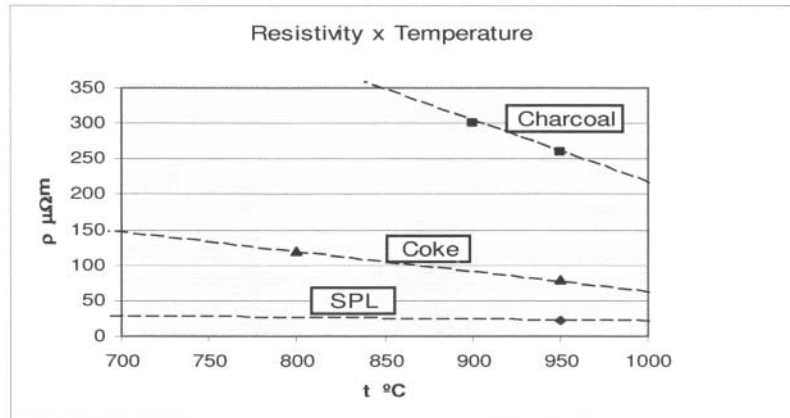


Figure 7. Resistivity dependence with temperature – Selected reducing agents

According to the above figure, SPL resistivity is the lowest when compared to coke and charcoal. However, it must be pointed out that the figure from SPL corresponds to one resistivity whereas those from coke and charcoal are bulk resistivity's. This suggests that the SPL bulk resistivity, considering the same particle size of that as coke, would be very close to that of this later.

#### Concluding remarks

The results of the simulations and other features carried out in this work suggest that, in principle, the employ of SPL's First Cut as an auxiliary reducing agent (with additional fluxing characteristics), is a technically feasible possibility.

This is a preliminary conclusion based on simulations that must be confirmed by industrial tests and that impact on other parameters such as environment and economics must be investigated. Initial exploratory industrial tests were made and the results, although essentially qualitative, are promising.

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