LADLE FURNACE SECONDARY METALLURGICAL PROCESS. DESULPHURIZATION OF FERRONICKEL, HIGH SULFUR CONTENT (0,5% a 1,0%)[1]

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Abstract

Increasing demand on stainless steel series 300 from world´s industries has motivated to former ferronickel producers to optimize their plants and attract new investors to participate in the market. Crude ferronickel from lateritic ore, reduced in electrical furnaces, contains high sulfur levels that can be removed with secondary metallurgical processes. The oxidation process takes place in a ladle (silicon, carbon and phosphorus) with a blowing station. The desulphurization and final chemical composition adjustment and heating for the final casting (ingots or granules), is performed in a ladle furnace station. This proven technology has direct influence on the unitary cost of the ferronickel production, when used efficiently. This paper describes the crude ferronickel refining stages with high sulfur content (0.2%-0.8%), with less cycling time and reducing operative costs using FeSi.

Key words: Ferronickel; Desulfurization; Ladle furnace; Ferroalloys.

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1 INTRODUCTION

The increasing worldwide demand of austenitic stainless steels during the last decades with an annual growing rate of 5.9% from 1950 to 2010,[1] has incentivized the ferroalloys producers[2,3] to increase the production and allow other investors to develop new projects on different places around the world.[4-6] All of them are directed to increase the ferronickel production (FeNi). The FeNi is produced from nickel lateritic ore with 1.6%-2.1% of Ni content. The ore, extracted from open pits, is homogenized, dried, calcined and finally reduced on an electrical furnace. The sulfur content on the nickel ore is associated to the iron oxides with a pyritic form and it cannot be removed during the reduction process. Then the percentage of sulfur in the crude FeNi is very high in most of the reduction process (Table 1).

Table 1. Percentage of sulfur from some crude FeNi producers

Smelter	%Ni	%Co	%Si	%C	%P	%S	Others	%Fe	Tap °C
ANEKA	19 - 22	0.3	2.4	1.8 - 2.4	0.021	0.25	1.0	N/D	1450 -1500
Barro Alto	28 - 32	< 0.7	< 0.03	< 0.30	< 0.05	< 0.30	1.0	N/D	1450 -1490
CMSA	33 - 35	< 0.9	< 0.03	< 0.025	0.035	< 0.65	1.0	Bal	1440-1460
Loma	20 - 24	< 0,50	< 0.05	< 0.050	0.046	0.5 - 0.8	1.1	N/D	1471 -1530
Onça Puma	33 - 36	< 1.1	< 0.05	< 0.050	0.045	0.5 - 0.8	1.0	Bal	1470 -1530
Posco	20 - 22	< 0.70	0.1	1.6 - 2.0	< 0.03	0.5	1.0	N/D	< 1550

Source: ERAMET, ANEKA, LOMA, and Personal notes.

So, to satisfy the market requirements (technical specifications), crude FeNi must have a secondary refining process on a ladle furnace, following an oxidation, desulphurization, heating and final adjustment chemical composition (Table 2).

Table 2. Sulfur percentage required by main costumers

%Ni	%Co	%Si	%C	%P	%S	Others	%Fe
18-36	max 1.1	< 0.7	<0.030	<0.030	< 0.030	1.0	Bal

Source: ERAMET, ANEKA, LOMA, and Personal notes

1.1 Objective

The objective of this paper is to desulfurize crude FeNi from reduction electric furnaces with sulfur percentage greater than 0.2%, using FeSi as a deoxidizer. Aluminum is commonly used in this process but due to instability price and operational problems associated with obstruction of ladle bottom slide gate and tundish nozzle during granulation casting (clogging).[7] Then FeSi is a good option to achieve this objective.

1.2 Literature Review

The nickel oxides, lateritic ore[8] constitute a very important part of nickel's world reserves. Nickel ore deposits are very heterogeneous with respect to their chemical composition; therefore a pyro metallurgical process was performed to produce crude FeNi.[9] Crude metal is tapping from the electric furnaces at temperatures between 1.440°C to 1.510°C, depending on the selected reduction process oxidation or reduction process. The usual chemical composition from that process is shown on Table 3.

Table 3. Percentage of sulfur required by main costumers

Process	temp tap °C	% Ni	% Si	% C	% P	% S	Others	% Fe
Oxydation	1460 - 1510	16-35	< 0.1	< 0.1	< 0.06	< 1.0	1.0	Bal
Reduction	1420 - 1500	16-36	< 1.5	< 0.5	< 0.06	< 1.0	1.0	Bal

Source: ERAMET, ANEKA, LOMA, and Personal notes

The nickel grade in alloy depends directly on the Fe/Ni ore ratio, while the silicon and carbon are related with selected smelt process (oxidation or reduction). Huge sulfur quantities on the metal came from the sulfur present in the ore, associated to iron (Fe) in pyrite forms (FeS2), without taking into account sulfur contributed by the coal to reduction and sulfur in electrode paste. High ore sulfur´s percentage is incorporated to the molten metal during the fusion in the electric furnace.

Then, the refining process and equipments for each project are defined taking into account the characteristics of the crude FeNi to produce, and the requirements of customers in relation to the final product.

In this study we will not analyze the theory concerning the process of removing impurities from molten FeNi (Si, C and P), discussed extensively in other studies related to steel refining [10] and crude FeNi.[11]

Experimental studies by Richardson and Fincham[12] and Denier,[13] have demonstrated that using lime (CaO) in the desulphurisation process with top slag as reagent for the molten steel is achieved to fix the sulfur in the slag; equation 1.

$$M_o.\underline{S} + (CaO)\mathit{Slag} \rightleftarrows M_f + (CaS)\mathit{Slag} \qquad (1)$$

In the FeNi case and following the theory,[11] the results were the same, taking into account that molten FeNi behavior is similar than molten steel. Then, we were able to eliminate large amounts of sulfur from crude FeNi, if the metal remains deoxidized, equation 2.

$$(M_a)\mathit{Desoxidante} + M_o.\underline{S} + (CaO)\mathit{Slag} \rightarrow M_f + (CaS)\mathit{Slag} + M\mathit{Oxidos} \qquad (2)$$

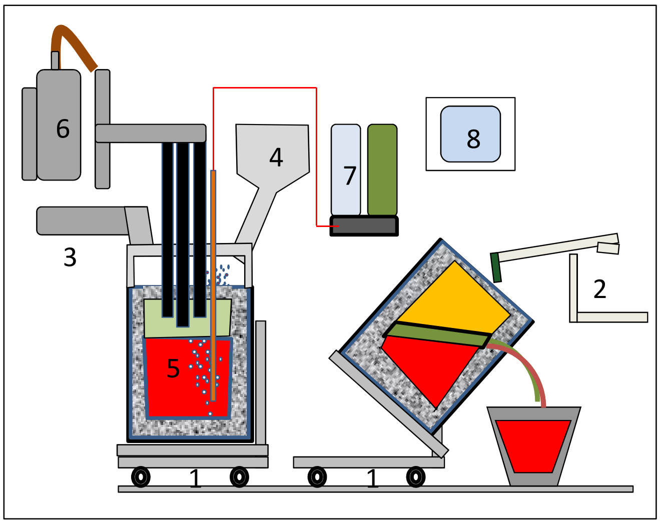
- M_a: alloy or deoxidized metal;
- M_o: crude metal (FeNi);
- M_f: refined metal;
- M_{Oxidos}: oxides formed;
- *Slag:* slag.

We have not seen a favorable or unfavorable influence in relation to the nickel´s percentage in ferronickel (FeNi), to remove sulfur.

2 MATERIAL AND METHODS

This study was conducted in a series of crude FeNi heats casting from a 12 MW electric furnace. The metal casting at 1.450°C ± 10, in a 10 tons ladle (MgO lining refractory). Then, molten metal is transferred to the refining station for processing (Figure 1).

2.1 Equipment



1 Ladle car (10 t);
2 Skimming station, sampling and testing temperature for molten metal;
3 Gas cleaning system;
4 Hopper for feeding mixture lime (CaO+MgO), fluor spar, FeSi and CaSi.
5 Ladle with MgO bricks (10 t);
6 Electrical arc furnace with heating station (3 MVA transformer) ;
7 Nitrogen and oxygen lance for oxidation and stirring;
8 All equipment can be controlled from a main board connected by PLC.

Figure 1. Ladle furnace equipment.

This process, similar to the steel's refining on a ladle furnace and has been successfully implemented in FeNi refining process by ASEA–SKF[14]. and SMS-Concast AG.[15]

2.2 Refining FeNi Process

The secondary refining process is divided in three phases.

2.2.1 Oxidation

The oxidation process to reduce silicon, carbon, and phosphorus is performed in a blow station using a refractory lance to blowing oxygen at 10 bars to 14 bars and 15-20 Nm^3/min.

2.2.2 Desulfurization

We use the following procedure to remove sulfur:

- after oxidation, the Fe Ni is killed adding FeSi, and the slag must be removed (skimming station) The dissolved oxygen in the molten metal shouldn´t be higher than 10 ppm.
- to increase temperature of the molten metal before desulfurization, FeNi must be higher than 1.600°C, using ladle furnace to heat.
- the slag prepared to desulfurize must have a low melting point (T_{liq} <1.570°C). With CaO between 55%-60%; MgO between 8-10; CaF_2 between 5%-10%, SiO2 between 5%-10%; Al2O3 between 15%-25%, and maintain iron oxide lower than 5%;
- dissolved oxygen on the molten metal ($\underline{O}$) before starting desulfurization must be less than 5 ppm;
- molten FeNi, must always remain deoxidized during the desulfurization stage and, stirrer with blowing nitrogen using refractory lance with 10 bars to14 bars and 2-3 Nm^3/min.

2.2.3 Final adjustment for casting

Final specifications for the sulfur in the FeNi are achieved by CaSi[16] (core wire) injection. The efficiency of the wire injection is good and the reaction is instantaneous. We recall that desulfurization is performed if the metal is completely deoxidized. To obtain the temperature required for casting granules 1.630°C ± 10, the FeNi is heating by the ladle furnace.

3 RESULTS

Following the explained procedure and taking into account the basic conditions to desulfurize crude FeNi, the following main results were obtained:

With a FeNi temperature more than 1.600°C, the slag prepared with the mixture of lime, dolomite and flour spar in the appropriate proportions, it melted easily, with the aid of a top refractory lance like stirring device.

Also, it was possible to maintain the FeNi and slag deoxidized, controlling the dissolved oxygen percentage with additions FeSi ferroalloy.

In the majority of heats processed, with the first desulfurizing treatment was achieved values of sulfur in the metal less than 0.1%, with a desulfurization rate higher than 85% (Figure 2).

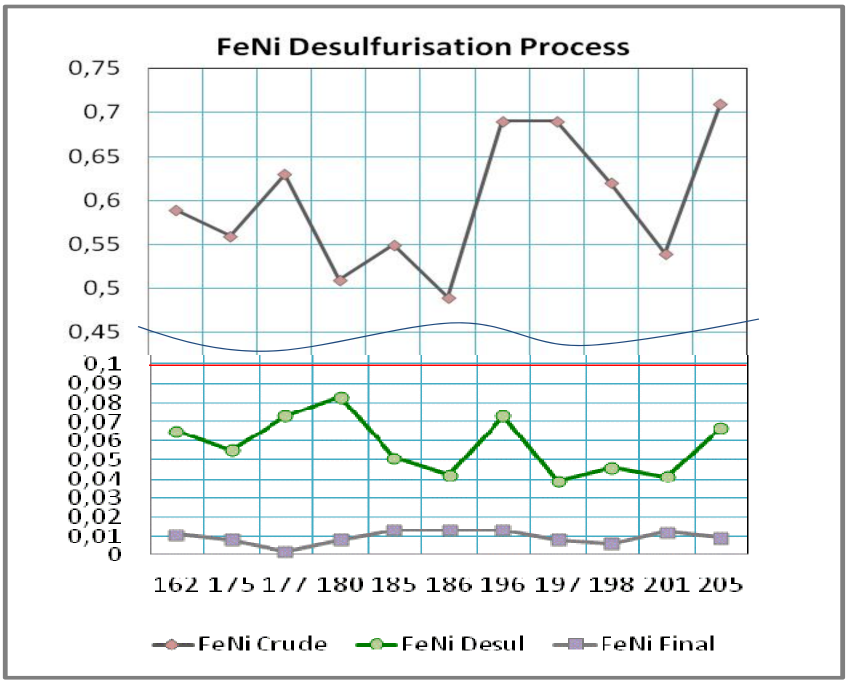


Figure 2. FeNi desulfurization process. Source: PGMC, FeNi data process.

The time to remove the sulfur from FeNi was less than 15 minutes. It was found that with sulfur percentages less than 0.06%, the reaction kinetics is very slow, because the slag is cooled very quickly. Figure 3 represents the sulfur percentage reduction vs. time in minutes, taking a series from five heats.

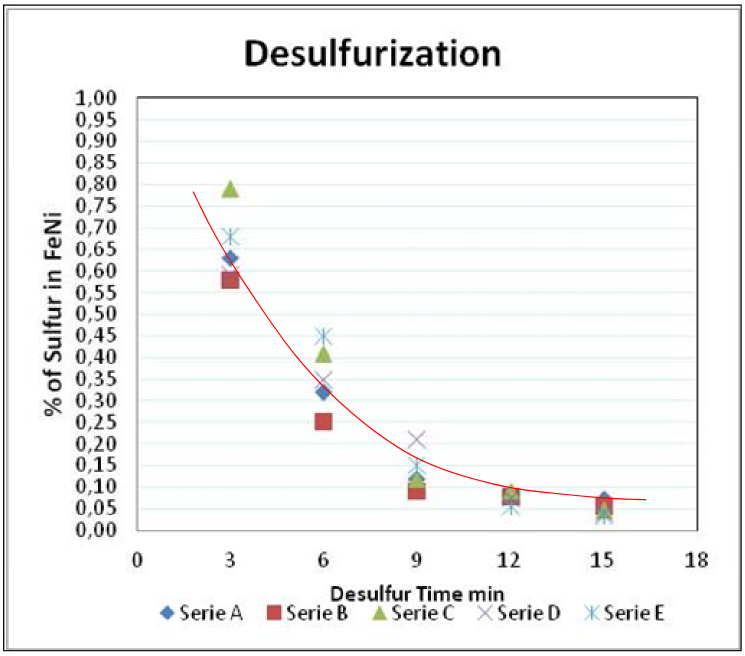


Figure 3. Sulfur reduction vs. time in minutes. Source: PGMC, FeNi data process.

Figure 4, shows the evolution of color of slag during the desulfurization process, changing from dark to black with the processing time.

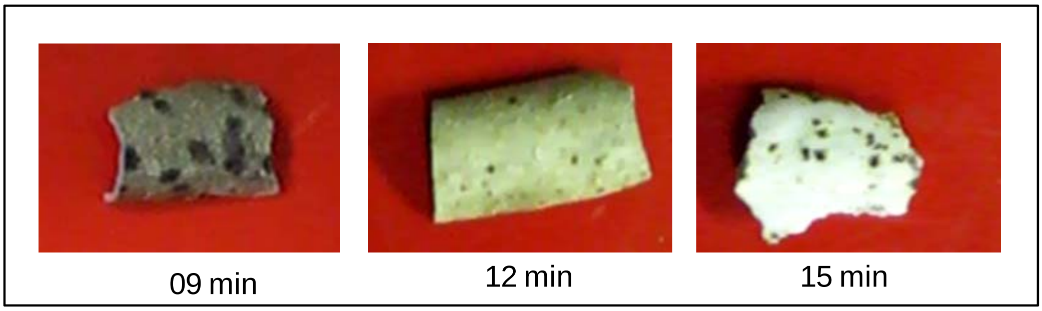


Figure 4. Heat 197 desulfurization slag. Source: PGMC, FeNi data process.

With the addition of wire CaSi, sulfur remaining on the FeNi, decreased from 0.08% to less than 0.030%; achieving customer specifications. The chemical analyses of the slag are shown in Table 4.

Table 4. Desulfurization slag chemical composition

Heat	Al2O3	SiO2	CaO	MgO	SO3	P2O5	FeO	Ni
162	6,62	19,71	50,18	14,39	0,75	0,02	2,11	0,23
175	10,81	13,36	58,05	9,58	1,01	0,02	1,21	0,41
177	9,73	10,87	61,74	7,20	0,51	0,21	2,87	0,35
180	9,47	12,74	60,59	8,24	9,81	0,05	0,97	0,29
185	5,05	25,39	58,51	8,23	2,55	0,05	1,04	0,13
186	12,16	9,67	60,47	7,93	16,22	0,02	0,29	0,07
196	12,63	9,54	59,87	5,90	17,39	0,11	1,16	0,13
197	9,22	15,41	58,81	7,75	3,34	0,02	0,57	0,06
198	9,09	13,51	61,14	7,37	5,64	0,02	0,25	0,07
201	8,78	15,99	60,35	9,03	1,19	0,03	0,47	0,07
205	13,06	6,42	62,95	7,80	3,84	0,05	1,73	0,15

Source: PGMC, FeNi data process.

The final chemical composition of FeNi to casting at 1.630°C ± 10 (ingots or granules), is shown in Table 5.

Table 5. Slag desulfurization

Heat	Al	Si	P	Ni	Co	C	S	Fe
162	0,017	0,498	0,015	22,14	1,027	0,02	0,011	75,47
175	0,061	0,436	0,023	20,88	1,027	0,017	0,008	76,95
177	0,016	0,314	0,009	22,215	1,068	0,024	0,002	75,75
180	0,01	0,268	0,006	21,94	1,058	0,018	0,008	75,71
185	0,007	0,292	0,007	21,66	1,058	0,018	0,014	76,06
186	0,038	0,317	0,011	20,979	1,042	0,02	0,013	76,80
196	0,1	0,289	0,012	20,511	1,037	0,022	0,019	77,43
197	0,021	0,317	0,003	22,22	1,089	0,02	0,008	75,64
198	0,13	0,332	0,014	19,916	1,038	0,024	0,006	77,74
201	0,024	0,34	0,012	20,34	1,053	0,023	0,012	77,62
205	0,021	0,346	0,014	20,88	1,062	0,016	0,001	76,78

Source: PGMC, FeNi data process.

The above process is summarized in Figure 5. The total cycle time to refining FeNi not includes casting from reduction electrical furnace and oxidation process, because this step is performed in a different station and doesn't affect the refining station occupancy.

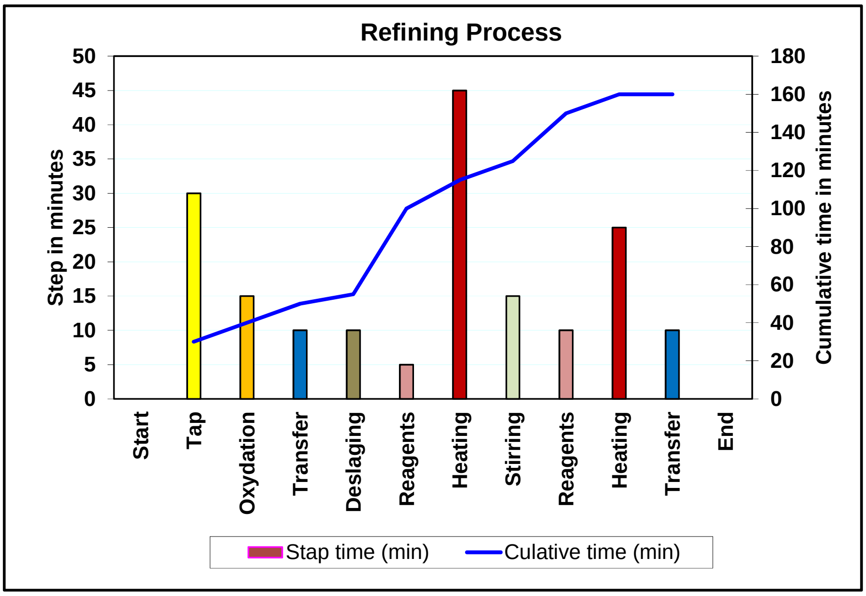


Figure 5. Summarized FeNi process. Source: PGMC and personal notes.

The total desulphurization time process, adjusting the chemical composition and temperature is on the order of 120 minutes. This process has been achieved to desulfurize FeNi with high sulfur percentage in less than 120 minutes until the specifications required by customers (Table 5).

4 DISCUSSION

Crude FeNi from a reduction furnace is processed in a ladle (10 t) with basic refractory line (MgO). The first stage is performed in a separate oxygen blow station. The basic stages of the process are done in the same ladle station, desulfurization and adjustments of chemical composition and heating for the casting.

With the deoxidized molten FeNi (ppm O < 10), it's guaranteed that the FeO percentage on the slag is lower than 5%. This condition allows the stability of the desulfurization slag; Equation 2.
With temperatures above 1.600°C in the molten FeNi, achieved by the ladle furnace, we can maintain slag with high temperature and good fluidity to fixing sulfur (CaS) in the slag. Also, it must be take into account that the temperature of the tapped metal from the reduction electrical furnace is relatively low compared with the temperature to start the desulfurization treatment (more than 180°C), and slag prepared to desulfurizing must have a melting point near to 1570°C.
In practice, the biggest difficulty to desulfurize FeNi with high sulfur percentage (S< 0.6%) is to fix the great sulfur amounts on the slag as calcium sulfite (CaS). The desulfurization reaction is so unstable that doesn't allow the CaS to stay on the right side of the Equation 2, if the metal or slag are oxidized.
As it was mentioned before, the lime mixture must be prepared with the adequate proportions to achieve a low melting point (T_{liq} < 1.570°C). Also, the amount of mixture of lime (CaO, MgO, SiO_2, CaF_2) to prepare the slag has a very important role. Lime in excess is needed to prevent saturation and to fix calcium sulfite in the slag. It is a good practice to avoid a halt on the desulfurization reaction.
It's very important to remember that the reaction moves to the right (Equation 2) only if the dissolved oxygen on the metal is in very low levels. This is achieved adding a deoxidized element in the bath. In this case, FeSi (stone or wire) can be used, depending on the market prices.
In order to facilitate the sulfur reaction in the metal with lime (slag) and taking into account that the reaction is realized on the slag-metal interface, the slag and metal must be stirred to promote chemical reaction.[17] It has been proven that the kinetics reaction is very fast if the previous conditions are appropriate.
With this desulfurization process it's difficult to reach sulfur values lower than 0.06%. Taking into account the client's demands, the FeNi are lower than 0.030% of sulfur; it's necessary to continue a desulfurization process with profound CaSi wire injection. CaSi quantity to add, depend on the present percentage of sulfur in molten metal, and the amount of FeNi in the ladle (stoichiometry calculation).
Finally, for casting (ingots or granules), FeNi is heating up to proper temperature. (1.630°C $\pm$10).

5 CONCLUSIONS

- FeNi temperature above 1.600°C promotes slag fusion and provides stability of CaS in the slag;
- control of the dissolved oxygen in the metal is critical for the desulfurization process development. The reaction does not continue if the dissolved oxygen percentage in the metal is greater than 10 ppm;
- the desulfurization reaction rate is very fast and decreases exponentially when reaching values close to 0.1% sulfur in the FeNi. As the sulfur percentage in the FeNi is lower, it is harder to remove with this procedure;
- with this procedure, crude FeNi has been desulfurized with high percentage of sulfur (0.20%> S <0.80%) in less than 120 minutes, achieving the technical specifications for customers.

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