

# The Influence of Gangue and Additives on the Divalent Iron Content of Magnetite Pellets

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During the pyroconsolidation of magnetite pellets in an aerobic atmosphere, the mineral practically oxidizes in the beginning stages of the process. However, as the temperature increases, the hematite dissociates into magnetite. The temperature at which this phenomena occurs depends on the additives present and is significantly lower than that corresponding to pure magnetite. In this paper a series of magnetite pellets were formed, varying the alkalinity  $(\text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$  from 0.4 to 1.9, and the  $\text{MgO}/\text{CaO}$  ratio from 0.12 to 1.3. The pellets were pyroconsolidated at temperatures ranging from 1050 to 1350°C. Pellet structure was determined and analyzed using electron microscopy. The influence of additives and gangue composition was studied at the hematite disassociation temperature.

## 1. Introduction

The quality of pyroconsolidated pellets for ironmaking and their behavior in the blast furnace are essentially determined by their  $\text{Fe}^{2+}$  content; that is, the higher the  $\text{Fe}^{2+}$  content, the lower the quality of the pellets concerned. The heating (pyroconsolidation) step involved in the making of magnetite pellets, which is intended to convert magnetite into hematite, must be carried out in an oxidant atmosphere; however, pyroconsolidated pellets occasionally contain substantial amounts of divalent iron ( $\text{Fe}^{2+}$ ) despite the oxidizing conditions used. The presence of ferrous iron in the pellets is usually ascribed to deficient oxidation of the original magnetite via the effect of liquid slag that covers the mineral grains during the process. In fact, on increasing the temperature to a sufficiently high level, the process is reversed and hematite is converted back to magnetite through the following thermal dissociation reaction:<sup>[1,2]</sup>



Pellets obtained from magnetite with an  $\text{Fe}^{2+}$  content of 24% lose more than 95% of ferrous iron on oxidation in the

early stages of pyroconsolidation.<sup>[3,4]</sup> When the temperature exceeds 1392°C ( $\Delta G^\circ(T=1392^\circ\text{C})=0$  to the reaction-equilibrium (1)) results in the opposite reaction and the hematite dissociates into magnetite and oxygen. The temperature at which the above phenomenon occurs (equilibrium (1)) is influenced by pellet composition ( $\text{SiO}_2$ ;  $\text{Al}_2\text{O}_3$ ;  $\text{MgO}$ ;  $\text{CaO}$ ; and  $\text{K}_2\text{O}$ ) and is always significantly lower than the thermodynamically predicted temperature for pure magnetite: 1392°C.<sup>[5]</sup>

The purpose of this paper is to study a set of phenomena that occurs during the pellet pyroconsolidation phase, in order to be able to draw general conclusions and, at the same time, lay the groundwork for resolving problems that may arise when pyroconsolidating pellets in the future. Especially of interest are: First, the oxydation process of the magnetite during the beginning stages of the heating process; second, the thermic decomposition process of the hematite thus formed, depending on temperature changes and additives; and third, the microstructural changes in the pellets across the thermic profile, the mechanisms of formation of the microconstituents and their characterization.

## 2. Experimental Process

The pellets used for this project were prepared with magnetite ore obtained by magnetic separation in an aqueous medium. An average of the analysis results of the ore and additives are given in **Table 1**. The concentration of magnetite in the ore studied was 94.8%. Ninety-nine percent of the ore was of a size smaller than 124  $\mu\text{m}$ .

In the formation of green balls, a granulating disc of 1250 mm in diameter was used. Once formed, the balls

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	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CO <sub>2</sub>	Fe total
Iron ore	0.54	0.52	2.20	0.40	0.054	0.052	–	68.7
Dolomite	35.14	15.95	2.78	0.5	0.035	0.030	44.3	0.5
Limestone	52.7	1.3	2.1	2.86	0.04	0.08	40.9	–
Magnesite	2.0	83.83	3.5	1.5	–	–	–	6.3
Silica	0.017	0.009	99.39	0.20	0.02	0.15	–	0.065

**Table 1.** Chemical analysis of ore and additives (wt%).

were sorted, and the ones with a size between 10 and 12 mm were used.

The series of pellets prepared is given in **Table 2** according to alkalinity and MgO/CaO ratio. The SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents remained quite similar. When a higher CaO content was required, limestone was added, and to increase the amount of MgO magnesite was added. When an increase in both was required, first dolomite was added, and then finer adjustments were made with either limestone or magnesite.

## 2.1. Pyroconsolidation

For this phase, 300 g of green pellets balls were put in a ceramic crucible with a perforated bottom which was then placed in a furnace preheated to 125°C and allowed to dry for half an hour. Then the balls, still in the 125°C furnace, were subjected to a current of air, using a suction pump. The furnace was brought to the desired temperature and kept at that temperature for 20 min.

The flow of air used to oxidize the magnetite was much greater than theoretically required in order to compensate for leakage and maintain an oxygen-rich environment around the balls, thus guaranteeing complete oxidation.

In previous work carried out on the oxidation of magnetite,<sup>[6,7]</sup> the pyroconsolidation test conditions were set to ensure a theoretical guarantee of complete oxidation. For instance, the time needed for complete oxidation of a pellet 12 mm in diameter, which is surrounded by air at a temperature between 940 and 1025°C, is less than 15 min. However none of the work done explains pellet behavior at temperatures under 420°C.

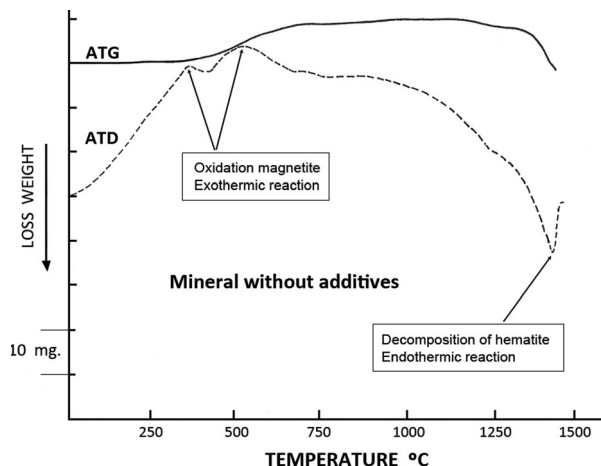
The thermogravimetric analysis done on the ore without additives (**Figure 1**) shows that weight gain in the sample begins at 300°C, and that when 420°C is reached the weight has increased by 10% of the total gain. This process is accompanied by an exothermic reaction which can be observed in the thermal differential analysis. The maximum weight is gained when the temperature reaches 1000°C.<sup>[7]</sup> Thus it can be deduced that in an atmosphere of air, magnetite begins oxidizing at 300°C and is completely oxidized at 1000°C. During the tests done, the furnace (conventional or solar) went from 300 to 1000°C in 55 min, more than enough time to completely oxidize the samples.<sup>[8]</sup>

## 2.2. Ferrous Content of Pyroconsolidated Pellets

In **Table 3**, the divalent iron, Fe<sup>2+</sup>, content of the pellets is shown. We can see that the Fe<sup>2+</sup> content remains constant

Alkalinity	MgO/ CaO	Name	Additives added (wt%)					Chemical composition of the pellets			
			SiO <sub>2</sub>	M	L	D	Total	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
0.4	1.3	P1-1	0.4	0.17	–	–	0.57	0.54	0.66	2.5	0.40
	1.0	P1-2	–	–	–	–	–	0.54	0.52	2.2	0.40
	0.7	P1-3	0.4	–	0.38	–	0.78	0.73	0.52	2.6	0.40
	0.5	P1-4	1.1	–	0.94	–	2.04	1.01	0.51	3.2	0.41
1.3	0.18	P4-6	–	–	4.63	–	4.63	2.90	0.55	2.3	0.43
1.9	1.3	P6-1	–	1.95	–	4.71	6.66	2.20	2.90	2.3	0.40
	0.12	P6-6	–	–	8.00	–	8.00	4.70	0.60	2.2	0.55

**Table 2.** Index of alkalinity, MgO/CaO ratio, additives (S: Silica, M: Magnesite, L: limestone, D: Dolomite), and pellet composition for the different pellets tested.



**Figure 1.** Thermogravimetric analysis of the ore without additives.

at temperatures of from 1050 to 1100°C, and the percentage corresponds to that of a completely oxidized pellet. At 1150°C a slight increase in the amount of  $\text{Fe}^{2+}$  can be seen, which dovetails with the increase in temperature.

In the table, we can see that greater alkalinity corresponds to a higher ferrous content. When alkalinity and temperature are kept constant, the divalent iron,  $\text{Fe}^{2+}$ , content, increases with an increase in the  $\text{MgO}/\text{CaO}$  ratio. There we can see that the temperature and alkalinity have a marked effect, playing an important role in the phenomenon of thermal dissociation. The  $\text{MgO}/\text{CaO}$  ratio acts similarly, indicating that of the two, the  $\text{MgO}$  content has a greater influence.

### 2.3. Microstructure Changes

The tests done show us what influence additives and  $\text{CaO}$  and  $\text{MgO}$  content have on  $\text{Fe}^{2+}$  content in pyroconsoli-

dated magnetite pellets, but in addition to that it would be useful to know how additives act during the heat cooking process of the pellets, in order to establish mechanisms of action that take place during the dissociation of hematite into magnetite (reaction-equilibrium (1)).

The study of pellet microstructure was carried out with a JEOL scanning electron microscope with a microanalyser which measures the dispersion of energy and wavelength. This equipment can provide quantitative analysis with an accuracy of 2%, using cobalt as the standard element.<sup>[9]</sup> The quantitative analyses which are presented in the tables are referred to as the oxides  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3$ . The contents appearing therein are presented without correction, as provided by the analytical team. When the sum of the contents exceeds 100%, this indicates that a part of the  $\text{Fe}_2\text{O}_3$  is found in the form  $\text{FeO}$ ; the more the sum of the contents exceeds 100%, the more  $\text{FeO}$  there is.

Especially close attention is paid to the pellets with relatively higher and lower alkalinity and  $\text{MgO}/\text{CaO}$  ratios, and examining the relationship between these values and the structural changes of the pellets. There are four classes of pellets that conform to these conditions: P1-4, P1-1, P6-1, and P6-6, to which must be added pellet P1-2, which corresponds to the ore without additives and is used as a reference to make comparisons.

## 3. Results and Discussion

### 3.1. Ore Without Additives (Pellet P1-2)

At the lowest temperature used in the study (1050°C), little change takes place in the pellet. There is no connection between the grains of hematite, either solid solution or molten slag; and their shape, with sharp corners and edges, tells us that the original structure is still present (Figure 2). As the temperature rises, the hematite grains become more

Alkalinity B	MgO/ CaO	Name	Temperature (°C)						
			1050	1100	1150	1200	1250	1300	1350
0.4	1.3	P1-1	0.27	0.28	0.27	0.60	2.98	3.50	7.30
	1.0	P1-2	0.26	0.26	0.26	0.26	1.77	2.94	4.84
	0.7	P1-3	0.38	0.38	0.40	0.45	1.63	3.00	3.53
	0.5	P1-4	0.35	0.37	0.41	0.60	0.95	1.35	5.78
1.3	0.18	P4-6	0.30	0.35	0.30	0.82	2.17	3.12	13.80
1.9	1.3	P6-1	0.55	0.50	1.44	4.18	10.40	10.47	14.98
	0.12	P6-6	0.58	0.60	1.17	2.03	3.51	6.05	13.30

**Table 3.**  $\text{Fe}^{2+}$  content in the pyroconsolidated pellets (wt%).

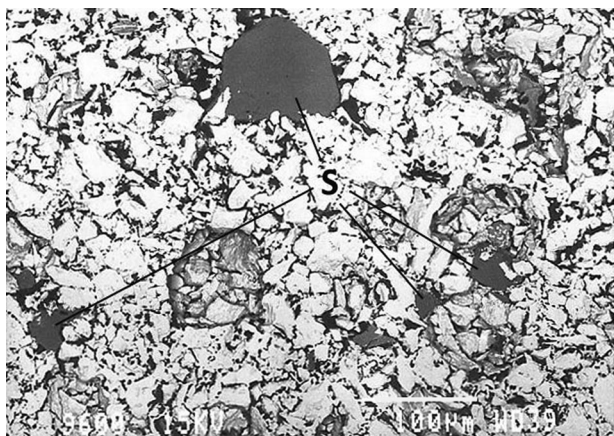


Figure 2. Pellet microstructure P1-2 at 1050°C. S, silica.

rounded and begin to join together, via solid solution or molten vitreous slag bridges. At 1300°C, practically all the grains have become globular (Figure 3). Upon quantitatively analyzing the grains, it is observed that at any of the temperatures studied, grains next to silica contain about 0.5% SiO<sub>2</sub>, while grains further away from the silica contain no dissolved SiO<sub>2</sub>. This indicates that it moves by diffusion, through quartz–hematite interface boundary contact, to the grains of iron oxide, forming a solid solution with a virtually constant concentration throughout the range of temperatures considered (Table 2).

As the temperature rises, gangue particles disappear, while at the same time the amount of intergranular vitreous slag increases. The particles melt together, forming intergranular slag; at 1200°C, the slag is quite uniform, while at 1300°C it is homogeneous throughout the pellet. One can see the variation in values that exist up to and including 1250°C. At 1300°C an important percentage of iron is in Fe<sup>2+</sup> form.

It can be observed that in Figure 3, at 1300°C, a few typical polygonal crystals appear, which as we will see

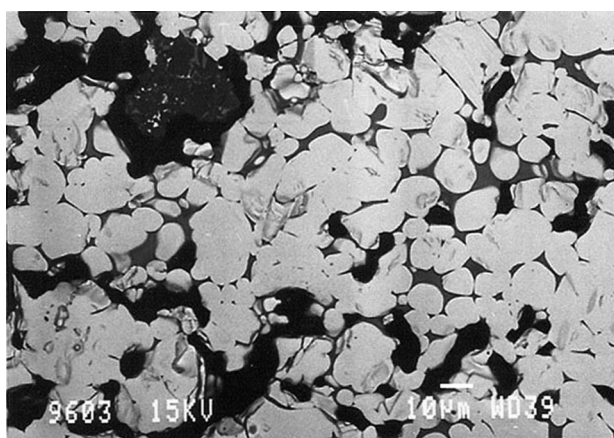


Figure 3. Pellet microstructure P1-2 at 1300°C.

	Temperature (°C)			
	1150	1200	1250	1300
MgO	8–20	1–5	2–3	3.4
CaO	11–0	4–15	12	16.8
SiO <sub>2</sub>	53–35	69–56	58–57	55.8
Fe <sub>2</sub> O <sub>3</sub>	23–24	13–18	24–23	20.4 <sup>a)</sup>
Al <sub>2</sub> O <sub>3</sub>	2–18	8–3	3–3	4.0
K <sub>2</sub> O	1–2	4–1	1–1	0.5

<sup>a)</sup>All or part of the iron is present as Fe<sup>2+</sup>.

Table 4. Slag composition for pellet P1-2 (wt%).

may mean a transformation of crystalline hematite to magnetite. Nearly all of them are rounded in appearance.

We know from the analysis done earlier that the hematite grains dissolve some silica. At this point it is impossible to say if that influences the appearance of Fe<sup>2+</sup>. What we can be sure of is that at 1200°C, all the grains, with or without dissolved silica, are at a state of maximized oxidation, and that at 1300°C a discrete amount of magnetite can be found in some, unrelated to whether or not dissolved silica is present.

We can see that the changes produced in the pellets are of two types. One is that as the pellets begin to heat, reactions occur which depend largely on the presence of gangue, with which slag of various compositions is formed. In addition, with this type of change, a high content of iron oxide is present, forming melted complex compounds which evolve with the temperature, while the greater part of the iron oxide in the hematite crystals are not in anyway altered at this point. So, the weight loss and appearance of Fe<sup>2+</sup> in the first phase is due to the formation of complex compounds in the gangue, in which part or all of the iron oxide may be present as FeO, forming olivine or wollastonite type compounds (Table 4).

When the temperature reaches 1300°C, or even when it is somewhat lower, there are already some crystals of hematite containing a little Fe<sub>3</sub>O<sub>4</sub>, while the slag, which contains a lot of Fe<sup>2+</sup>, is stabilized with a fixed composition. Therefore, we can say that the first appearance of ferrous iron is due to complex reactions of Fe<sub>2</sub>O<sub>3</sub> with the gangue, and that ferrous iron appearing after that, at temperatures of 1300°C and higher, is because of the dissociation of hematite crystals into magnetite.

### 3.2. Low Alkalinity and Low MgO/CaO Ratio (Pellet P1-4)

In Table 2, we can see that this pellet has been made with very few additives, so we would expect to see behavior similar to that of pellet P1-2 (ore without additives). At the

lowest temperature studied, 1050°C, and as in the case of P1-2, the pellet structure does not change. At 1100°C, the hematite crystals have incorporated into their structure a certain amount of the oxides present, but only when physical contact exists between the hematite grain and the oxide. Can be verified that the grains of hematite can solubilize up to 11.4% MgO when the slag in contact reaches a 23.0% MgO. At low temperature, the solid solution bridges are underdeveloped, randomly distributed, and only found in the presence of certain compounds. At higher temperatures, when all the hematite grains have bridges or contact with slag, they all have small quantities of oxides present, in greater or lesser amounts. These dissolved oxides play a part in the transformation of hematite to magnetite. At 1300°C, can be found, in contact with the slag, polygonal shaped pellets, and others who adopt globular morphologies. It can be seen that the globular crystals contain a small quantity of silica (0.3% SiO<sub>2</sub>), while the polygonal ones also contain CaO (0.3%) and MgO (1.6%); in the globular crystals the amount of magnetite found is small, while in the polygonal crystals it is considerably higher. This leads us to the observation that the slag, or certain components of it, influences the transformation of globular crystals to polygonal ones, and this change, as can be seen, is associated with thermal dissociation.

If the MgO and CaO content in the polygonal hematite crystals comes from the slag, then the concentration of these compounds in the slag is bound to decrease: MgO content in the centre of the slag is 1.5% and 0.3% in the edge, whereas for the CaO is 16.4% (centre) and 9.0% (edge). In **Table 5**, we can see the results of this analysis.

As can be seen in this table, the concentration of MgO and CaO is much lower at the edges than in the centre of the slag, which means the grains of hematite next to them act like sponges in regards to these compounds, which become part of the grains. The presence of these oxides in the hematite crystals accelerates the transformation of hematite into magnetite (Reaction (1)).

As for the slag, it also undergoes changes as the temperature rises; at first it is made up of particles of gangue of variable composition, and quartz grains, but

at 1100°C, one can see areas of change, albeit not many. Their average composition is shown in **Table 6**, next to the corresponding temperature.

The areas of intergranular slag spread as the temperature rises, so that by the time 1250 and 1300°C is reached, they are extensive. Quartz grains remain intact until relatively high temperatures, but there are fewer in this type of pellet than in the previous type, as in this case a small amount of limestone has been added (0.94%). This helps bring about the formation of calcium silicate with, as a consequence, the disappearance of a large proportion of the silica grains, which at 1250 and 1300°C are already difficult to find in our slag sample.

In **Table 6**, we can see that the MgO content decreases uniformly with the increase in temperature; this is because this compound is being absorbed by the hematite grains. One can also see a small decrease in the CaO content, but it is not as pronounced as in the case of the MgO. Silica undergoes a reverse process since it incorporates the quartz grains from the slag. The rest of the elements present do not appear to undergo any appreciable changes. It can be concluded that at the beginning of the process, neither slag nor hematite undergo much change. As the temperature rises, slags of variable composition are formed, while at the same time small quantities of SiO<sub>2</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub> dissolve in the hematite crystals, forming solid solutions. However this occurs only in those that are in physical contact with slag rich in those elements.

As the temperature rises, MgO and CaO both begin to dissolve in the hematite grains contiguous to the areas of slag which contain these oxides, especially MgO, for which they seem to have an extraordinary affinity; keep in mind that the atomic radius of Fe<sup>3+</sup> and Mg<sup>2+</sup> are similar (Fe<sup>2+</sup> 0.76 Å, Fe<sup>3+</sup> 0.64 Å, and Mg<sup>2+</sup> 0.65 Å). These oxides accelerate the transformation of hematite into magnetite, as shown in the analysis performed on the idiomorphic crystals which can be seen at 1300°C, keeping in mind that in this pellet the quantity of MgO and CaO present is not elevated. The reactions laid out

	Center (1)	Edge (2)	Hematite (3)
MgO	1.5	0.3	1.6
CaO	16.4	9.0	0.3
SiO <sub>2</sub>	53.0	65.0	0.4
Fe <sub>2</sub> O <sub>3</sub>	28.4 <sup>a)</sup>	23.0	100.5 <sup>a)</sup>
Al <sub>2</sub> O <sub>3</sub>	2.6	2.0	–
K <sub>2</sub> O	0.6	0.7	–

<sup>a)</sup>Part of the iron is found as Fe<sup>2+</sup>.

**Table 5.** Analysis of slag and hematite crystals (wt%).

	Temperature (°C)				
	1100	1150	1200	1250	1300
MgO	8.5	5.4	6.2	4.6	1.5
CaO	19.3	11.3	16.4	15.7	16.0
SiO <sub>2</sub>	40.3	39.5	55.4	53.2	55.3
Fe <sub>2</sub> O <sub>3</sub>	27.5	40.7	18.6	23.4	24.8 <sup>a)</sup>
Al <sub>2</sub> O <sub>3</sub>	3.5	1.7	2.4	2.0	2.5
K <sub>2</sub> O	0.5	0.5	0.5	0.5	0.6

<sup>a)</sup>Part is found as Fe<sup>2+</sup>.

**Table 6.** Slag composition at varying temperatures (wt%).

above only occur in the regions of the pellet where the content of these compounds just happens to be sufficient.

### 3.3. Low Alkalinity and High MgO/CaO Ratio (Pellet P1-1)

Our initial observation reveals that the change in pellet structure is slow, as is the case with the P1-2. At 1200°C, however, a large change can be seen, with numerous solid solution bridges between hematite grains, which are themselves more globular in appearance. Nearly all the small grains have disappeared, having joined together to make, or been incorporated by, large grains. Above this temperature, intergranular slag is present, and its volume grows along with the temperature (Table 2).

In Table 7, the slight increase in SiO<sub>2</sub> content becomes noticeable, as does the diminishing amounts of MgO and CaO oxides as they move towards the contiguous hematite crystals.

Figure 4 is that of an area of slag at 1300°C, whose composition is: 0.6% MgO; 20.8% CaO; 54.0% SiO<sub>2</sub>; 3.1% Al<sub>2</sub>O<sub>3</sub>; 0.3% K<sub>2</sub>O; 20.5% Fe<sub>2</sub>O<sub>3</sub>; one can see a black border which consists primarily of SiO<sub>2</sub>; and a gray mass of calcium silicate and some dendrites of SiO<sub>2</sub>·FeO. Composition of the polygonal grain of hematite contiguous to slag is as follows: 3.0% MgO; 0.2% CaO; 0.6%SiO<sub>2</sub>; 0.45% Al<sub>2</sub>O<sub>3</sub>; rest Fe<sub>2</sub>O<sub>3</sub> + Fe<sub>3</sub>O<sub>4</sub>.

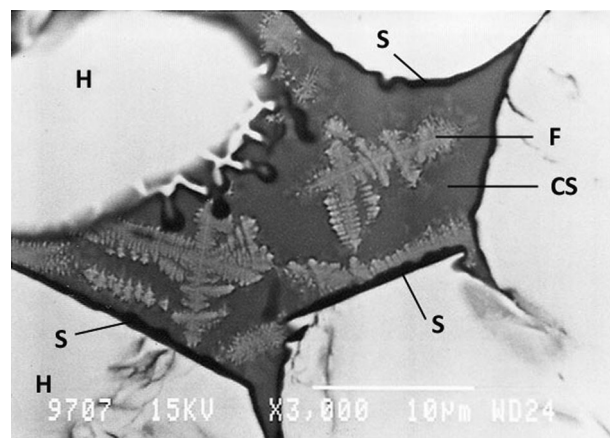
A quantitative analysis of the dendrite, expressed in atomic content, shows that for every 19 Si atoms there are 18.5 Fe atoms (the ratio is for all practical purposes 1:1) Since, on the other hand, most of the iron oxide present is in the form of FeO, it can be deduced that the dendrite consists of SiO<sub>2</sub>·FeO. The black areas around the border of the slag area in Figure 4 primarily consist of SiO<sub>2</sub>. This silica precipitated out as slag with a high silica content, situated in the tridymite range, according to the ternary diagram SiO<sub>2</sub>-CaO-FeO, cooled.<sup>[5]</sup>

The mechanism of the appearance of SiO<sub>2</sub> on the edges of the slag areas can be explained in the following way: at

	Temperature (°C)			
	1150	1200	1250	1300
MgO	8.3	4.5	3.0	1.0
CaO	15.3	15.0	12.3	8.2
SiO <sub>2</sub>	45.0	50.1	57.7	50.7
Fe <sub>2</sub> O <sub>3</sub>	28.0	25.0	23.0	38.4 <sup>a)</sup>
Al <sub>2</sub> O <sub>3</sub>	2.0	2.4	3.0	2.3
K <sub>2</sub> O	0.6	0.8	0.5	0.4

<sup>a)</sup>Part of the iron oxide is found in the form of magnetite.

**Table 7.** Slag composition at different temperatures (wt%).



**Figure 4.** Slag lagoon located in P1-1 at 1300°C. H, hematite, S, silica, F, FeO·SiO<sub>2</sub> dendrites, CS, calcium silicate.

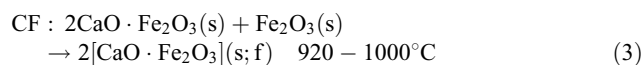
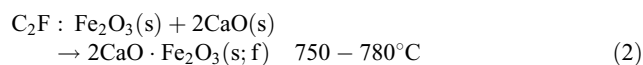
1300°C the intercrystalline slag is melted, magnesium having moved to the hematite crystals (0.6% in slag, 3% in hematite). The pellet begins to cool towards the exterior, so that heat leaves the slag areas through the hematite grains that surround them. The silica begins to precipitate from the coolest zones in the form of tridymite, that is, at the slag/hematite interface. In the centre of the slag we find concentrated liquid, the material with the lowest melting point, which solidifies in dendrites of SiO<sub>2</sub>·FeO in a matrix of SiO<sub>2</sub>·CaO.

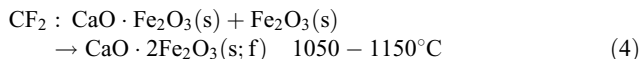
### 3.4. High Alkalinity and Low MgO/CaO Ratio (Pellet P6-6)

In the preparation of pellet P6-6, 8% of CaO was added (Table 3). During pyroconsolidation of the pellet, the limestone reacts with iron oxide to form ferrites (Table 2).

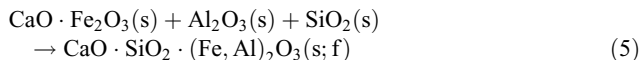
At 1050°C it is observed that, neither silica grains nor gangue is observed, which leads to the deduction that they have reacted with the additives. We do, however, observe the presence of crystallized ferrites (12.5% CaO; 5.2% SiO<sub>2</sub>; 0.45% Al<sub>2</sub>O<sub>3</sub>; 81.5% Fe<sub>2</sub>O<sub>3</sub>) in the form of needles or small plaques, along with the hematite crystals (0.6% CaO; 0.6% SiO<sub>2</sub>; 98.5% Fe<sub>2</sub>O<sub>3</sub>).

It has been determined<sup>[5,10]</sup> that the first ferrite formation reactions take place as solid–solid reactions, beginning at 750–780°C and continuing up to 1200°C, which is the melting point of these ferrites, according to the following sequence: dicalcium ferrite (C<sub>2</sub>F) → calcium ferrite (CF) → calcium diferrite (CF<sub>2</sub>).





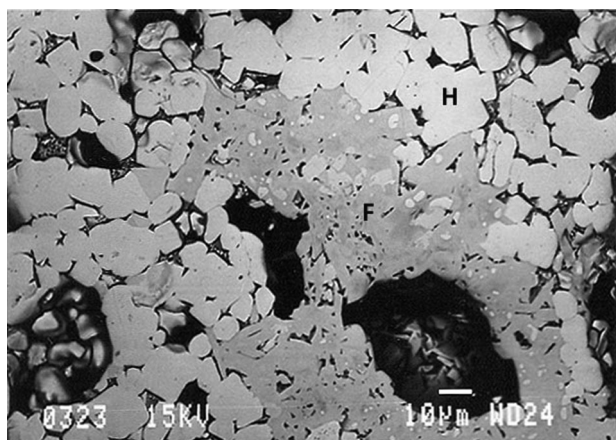
Simultaneously, at  $\approx 1050^\circ\text{C}$ , solid–solid ferrite forming reactions begin to occur, especially silicoferrites of calcium and aluminum (SFCA), which continue as solid–liquid reactions at higher temperatures. The presence of  $\text{Al}_2\text{O}_3$  increases the stability of SFCA and decreases the temperature at which these ferrites begin to form. Solid–liquid reactions predominate, with the presence of the molten phase which reinforces the assimilation of material to form SFCA type ferrite:



The formation of  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$  at  $1000^\circ\text{C}$  from a stoichiometric mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{CaCO}_3$  has been studied.<sup>[5,11]</sup> The  $\text{Fe}_2\text{O}_3$  reduces to  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$  before the calcination of limestone begins, as a function  $p\text{O}_2$ , which is determined according to the CO content in the reducing mixture  $\text{CO} + \text{CO}_2$ . We find the following order of reaction speeds of iron oxide with lime, for the formation of dicalcium ferrite ( $\text{C}_2\text{F}$ ):  $\text{FeO} > \text{Fe}_3\text{O}_4 > \text{Fe}_2\text{O}_3$ .

In one study, samples of calcium ferrite (CF),  $\text{CF} + \text{Al}_2\text{O}_3$  and  $\text{CF} + \text{SiO}_2$  were synthesized.<sup>[12]</sup> It was determined that the addition of alumina was more effective to dissolve the hematite in CF, while the addition of silica was more effective to increase the speed of formation of CF.

In another study,  $\text{CF}_2$  and samples of  $\text{CF}_2 + \text{Al}_2\text{O}_3$  (3–9%) +  $\text{SiO}_2$  (1–7%) were synthesized in order to make SFCA.<sup>[13]</sup> The evolution of these processes was followed via XRD. The solubility of alumina in  $\text{CF}_2$  at  $1250^\circ\text{C}$  is 5–7% and the solubility of silica is 2–4%. The monoclinic structure of  $\text{CF}_2$  changes to a triclinic structure when it reacts with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  to form SFCA.



**Figure 5.** Pellet microstructure P6-6 at  $1150^\circ\text{C}$ . H, hematite; F, ferrite.

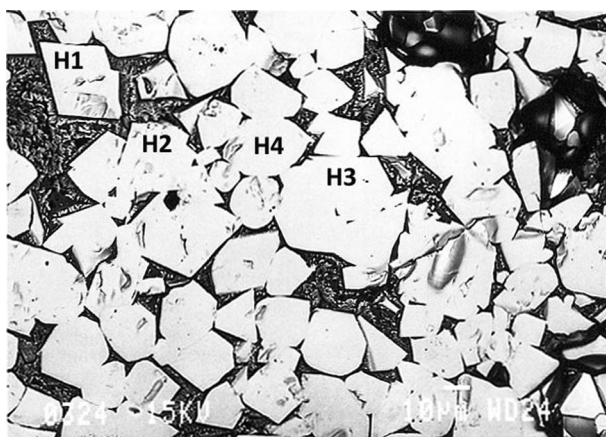
(°C)	MgO	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
1100	1.5	11.5	5.6	80.0	1.2
1150	1.3	11.3	5.7	79.2	1.4

**Table 8.** SFCA Composition (wt%).

At a temperature of  $1150^\circ\text{C}$  a larger ferrite presence is observed in the pellet structure (Figure 5). Table 8 reflects the composition of SFCA for temperatures of 1100 and  $1150^\circ\text{C}$ . The incorporation of MgO in the composition of ferrite can be seen. In Figure 8 more bridges between the grains of hematite can also be seen, as well as more globular shapes, and that smaller grains have joined together or been gathered up by larger grains.

At  $1250^\circ\text{C}$  the pellet structure has undergone drastic changes to its morphology, with more polygonal hematite crystals and intergranular slag with a unique appearance (Figure 6). The grains of hematite have quite varied compositions: those which are in contact with areas of slag contain dissolved oxides, most commonly CaO and  $\text{SiO}_2$ , while MgO and  $\text{Al}_2\text{O}_3$  are also found. On the other hand, more isolated grains have only CaO and  $\text{SiO}_2$ , in lower proportions, and a few have no dissolved oxides whatsoever (Table 9).

In the grains of hematite in contact with slag, part of the iron oxide present has been transformed into magnetite, while the grains which are not in contact have either no or very few dissolved oxides. In the table you can see the transformation to  $\text{Fe}^{2+}$  in those crystals which contain MgO. We can see that grains H2 and H4 have almost the same amount each of  $\text{SiO}_2$  and CaO, but one has 0.4% MgO, while the other lacks this oxide. The result is that the crystal which contains MgO is further along the path to becoming magnetite. This confirms what has been seen in other pellets; the presence of solid solution compounds,

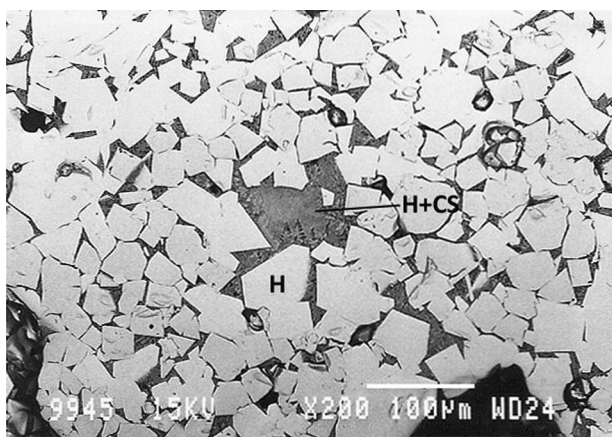


**Figure 6.** Pellet microstructure P6-6 at  $1250^\circ\text{C}$ .

	In contact with slag			No contact
	H1	H2	H3	H4
MgO	2.0	0.4	0.7	–
CaO	1.6	0.8	1.0	0.6
SiO <sub>2</sub>	0.3	0.5	0.4	0.5
Fe <sub>2</sub> O <sub>3</sub>	99.0 <sup>a)</sup>	100.0 <sup>a)</sup>	100.7 <sup>a)</sup>	99.0
Al <sub>2</sub> O <sub>3</sub>	0.4	–	–	–

<sup>a)</sup>Part of the Fe is found as Fe<sup>2+</sup>.

**Table 9.** Hematite grain composition at 1250°C (wt%).



**Figure 7.** Pellet microstructure P6-6 at 1300°C. H, hematite; CS, calcium silicate.

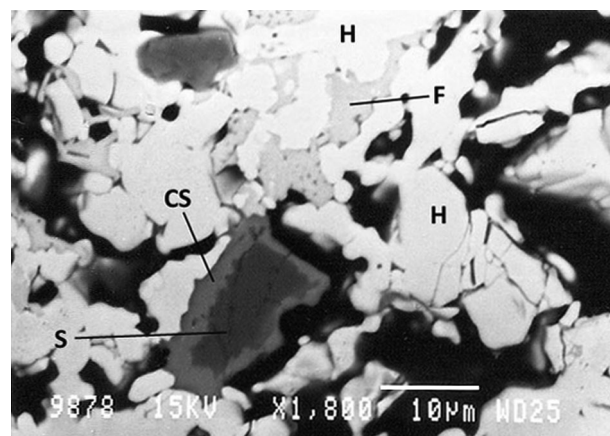
especially MgO, in a hematite crystal, accelerates thermal dissociation.

At 1300°C, one can see a greater number of idiomorphic hematite have dissolved almost all the compounds present. Two phases can be distinguished in the slag: calcium silicate (dark gray) and iron oxide in dendritic form (light gray) (**Figure 7**). Hematite composition (H) and slag (S) in the pellet P6-6 is as follows: (H): 0.7% MgO, 1.0% CaO, 0.3% SiO<sub>2</sub>, 0.4% Al<sub>2</sub>O<sub>3</sub>, Rest: Fe<sub>2</sub>O<sub>3</sub> + Fe<sub>3</sub>O<sub>4</sub>. (S): 13.0% CaO, 13.3% SiO<sub>2</sub>, 1.9% Al<sub>2</sub>O<sub>3</sub>, Rest: Fe<sub>2</sub>O<sub>3</sub> + Fe<sub>3</sub>O<sub>4</sub>.

We can observe that at this temperature the slag does not contain MgO, because, as we have already seen, hematite incorporates this oxide into its structure with notable facility.

### 3.5. Medium Alkalinity and Low MgO/CaO Ratio (pellet P4-6)

Limestone was added to this pellet, as in the case of pellet P6-6, albeit in a smaller percentage (Table 2). Figure 8 shows the structure of pellet P4-6 at 1050°C. We can see several phases; their composition is laid out in Table 10.



**Figure 8.** Pellet microstructure P4-6 at 1050°C. H, hematite; S, silica; F, ferrite; CS, calcium silicate.

	MgO	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
Hematite	–	0.2	0.4	99.0	0.4
Ferrite	3.0	11.0	7.0	76.0	3.0
Silica	–	–	97.0	3.0	–
Silicate	–	42.0	54.0	4.0	–

**Table 10.** Composition of localized phases in pellet P4-6 at 1050°C (wt%).

The silica grain (dark gray) located at the bottom part of the figure has reacted with CaO to form calcium silicate (light gray) which surrounds the grain. Limestone is used to make calcium silicates on the one hand and ferrite on the other, the formation of these two compounds occurs at very similar temperatures.

Ferrite begins to break down at ≈1200°C. At this temperature the ferrite undergoes a process by which the iron oxide has separated in alveolar form, or in the form of dendrites structures. At this point it is basically made up of crystals of CaO·SiO<sub>2</sub>, which contains some iron oxide as well as other gangue components. Therefore, in order to create a pellet with a structure that includes ferrite, one must add limestone so all the silica combines to form calcium silicate, and the temperature must be kept under 1200°C, so the ferrite does not break down.

In Figure 9, we can see the behavior of CaO in the transformations that occur during the pyroconsolidation of pellets with high or low alkalinity and a low MgO/CaO ratio. The initial appearance of ferrous content in ore to which limestone has been added begins at ≈1200°C, due to the thermal dissociation which happens in hematite crystals with an appreciable MgO content. This MgO,



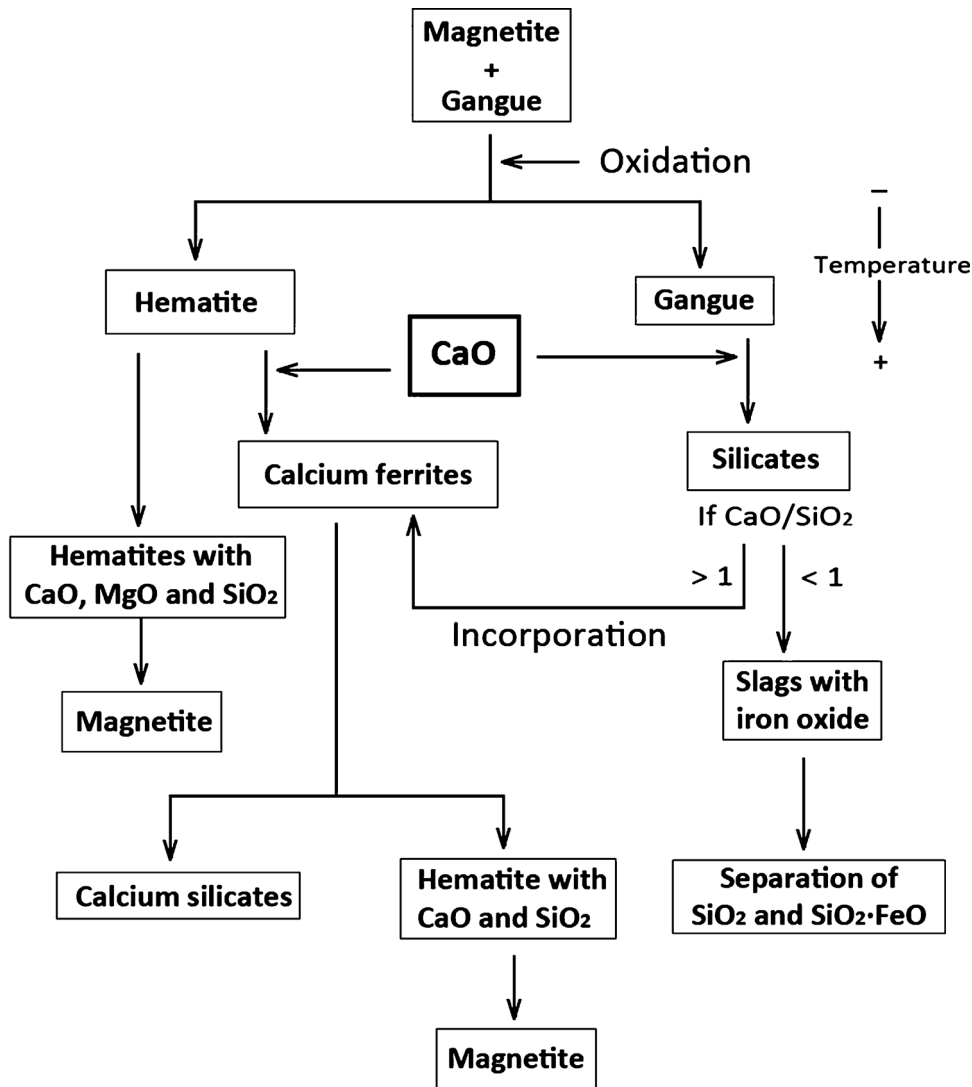


Figure 9. Behavior of CaO during pyroconsolidation.

which comes from the ore gangue, is found fixed solely to hematite crystals which are located contiguously to slag areas, said areas being depleted of MgO because of its affinity for the hematite crystals. This is due to the behavior of the additive CaO, which formed ferrites that quickly incorporated the gangue MgO into themselves. Finally these ferrites, abundant where there is elevated CaO, are the means by which MgO is able to reach neighboring hematite crystals.

### 3.6. High Alkalinity and High MgO/CaO Ratio (Pellet P6-1)

We have studied the influence of CaO on pellet P6-6 and established its role in hematite break down. Now we take a look at the behavior of MgO, which, as we have already seen, noticeably affects by its presence the appearance of  $\text{Fe}^{2+}$  during pyroconsolidation (Table 2).

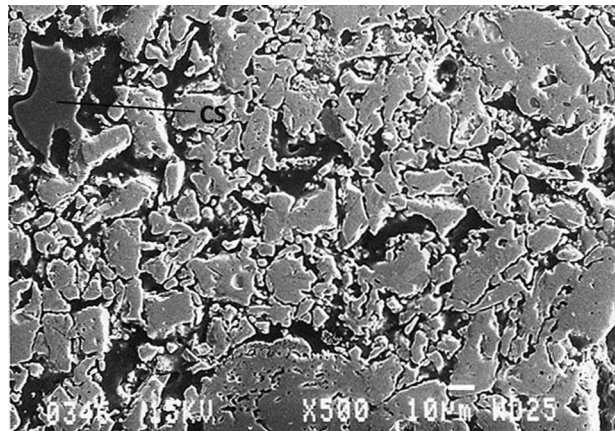
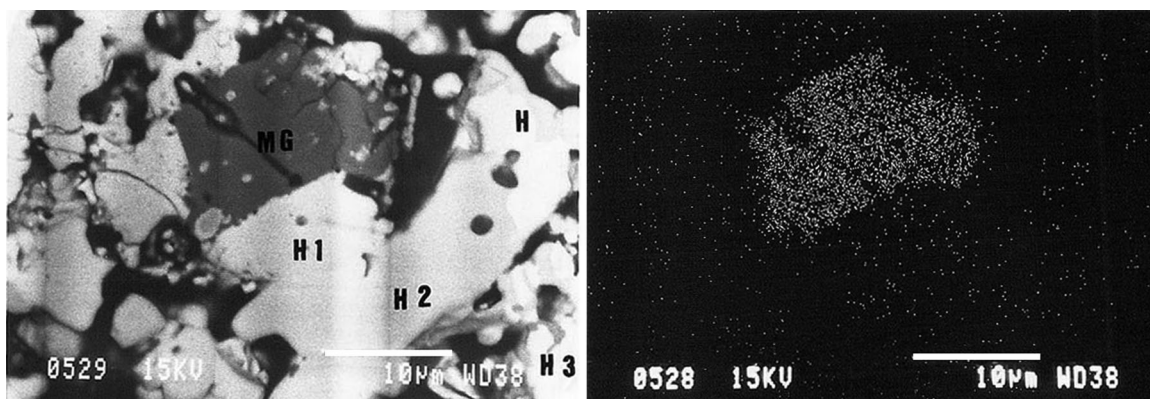


Figure 10. Pellet microstructure P6-1 at 1050°C. CS, calcium silicate.



**Figure 11.** A) Pellet microstructure P6-1 at 1050°C. MG, magnesium; H, hematite. B) Mapping of the magnesium corresponding to Figure 11A.

In P6-1, at a temperature of 1050°C, we observe that pellet structure is not much changed; the grains of hematite are still in their original form (Figure 10). In the structure, which appears heterogeneous, there are no silica crystals, which show that, as in the case of pellet P6-6, the additives have reacted with the silica to form silicates. In some areas we see particles from gangue, as in pellet P1-2; and magnesite crystals whose MgO content is 82–94%, and particles of magnesium silicate from the reaction between SiO<sub>2</sub> and MgO. There is no noticeable formation of vitreous slag at this point, due to the low mobility of the compounds at this temperature.

At 1050°C, to examine the influence of magnesite on hematite grains, the grains contiguous in a radial direction were studied, with the centre in the grain of magnesite. In Figure 11A, one can see the magnesite surrounded by hematite. Figure 11B, maps out the Mg present in the area of the previous figure. Table 11 shows the analysis of the magnesite and hematite crystals situated in positions 1, 2, and 3 (Figure 11A).

In this table we can see that part of the iron oxide has become ferrous, and the transformation is more marked when the content of MgO is higher.

Upon raising the temperature to 1200°C the magnesite crystals disappear completely, having dissolved into

	Magn.	H-1	H-2	H-3
MgO	87.8	16.3	14.6	12.6
CaO	–	0.5	0.4	0.4
SiO <sub>2</sub>	0.2	0.6	0.3	0.2
Fe <sub>2</sub> O <sub>3</sub>	12.0	84.1 <sup>a)</sup>	86.5 <sup>a)</sup>	86.8 <sup>a)</sup>
Al <sub>2</sub> O <sub>3</sub>	–	0.8	1.1	0.6

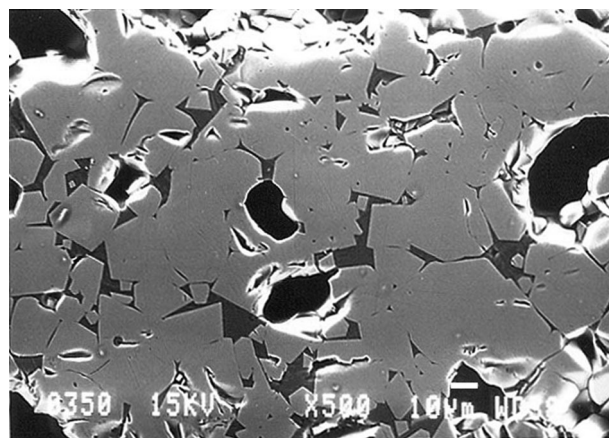
<sup>a)</sup>Part of the iron oxide is present as Fe<sup>2+</sup>.

**Table 11.** Composition of magnesite and hematite located in various zones, pellet P6-1 at 1050°C (wt%).

the hematite crystals. The crystals which are located contiguously to the slag areas, rich in MgO, and with an appreciable Fe<sup>2+</sup> content, are rounded in shape, although upon raising the temperature to 1250°C they present as rounded to polygonal in shape. Those hematite crystals which are further from slag areas, that is to say, not contiguous, and which for that reason contain no MgO, continue to present a rounded shape. At 1300°C crystals with a polygonal shape are more numerous and can be found in practically all areas of the pellet (Figure 12). The analyzes carried out on the pellets, demonstrate a close correlation between the presence of MgO and the thermal dissociation of hematite (reaction (1)).<sup>[5]</sup>

Slag as such is not found until a temperature of 1150°C is reached, at which point it appears is small, isolated areas. As the temperature increases, more slag can be seen, in clearly defined areas. The composition changes of slag are shown Table 12.

The amount of MgO present decreases steadily with the rise in temperature, while at the same time the number of hematite crystals which contain MgO grows. Thus, as has been determined in other pellets, hematite crystals have a



**Figure 12.** Pellet microstructure P6-1 at 1300°C.

	Temperature (°C)			
	1150	1200	1250	1300
MgO	3.3	2.1	1.7	1.0
CaO	31.3	30.1	28.0	29.6
SiO <sub>2</sub>	43.2	43.2	45.7	45.1
Fe <sub>2</sub> O <sub>3</sub>	18.2	22.5	22.1	22.0
Al <sub>2</sub> O <sub>3</sub>	1.5	1.5	1.6	1.5
K <sub>2</sub> O	0.4	0.5	0.7	0.5

**Table 12.** Slag composition (wt%).

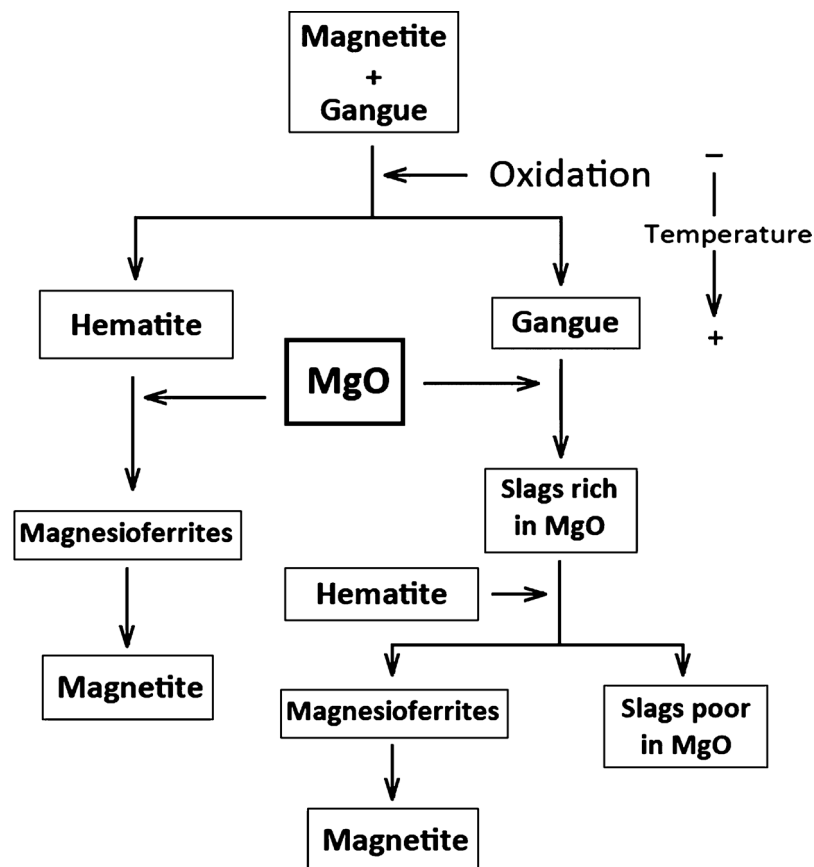
notable affinity for MgO, incorporating it into their structure. This MgO has a marked reducing effect on hematite.

When a pellet is treated, and the slag contains SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>,<sup>[14]</sup> when the Fe<sub>2</sub>O<sub>3</sub> is reduced, the result is peralkaline, SiO<sub>2</sub> · 2FeO, with a relatively low melting point of (1205°C). If MgO is added to the peralkaline slag, the FeO will precipitate out, causing an enrichment of MgO and increasing its melting temperature, which will result in

solidification. This allows the liquid state silicate fraction to decrease; in fact all the slag can be solidified in this way. In the literature,<sup>[15,16]</sup> there are many references to what occurs when MgO is present in slag, similar to what we have seen.<sup>[17]</sup> That said, when it comes to pyroconsolidated pellets, the effect of MgO is very small, for the reasons already mentioned. When the right temperature is reached, the MgO from the slag will incorporate into the hematite crystals, and its content thus notably decreases.<sup>[18–20]</sup>

Therefore the proposal to add MgO to increase the mechanical resistance of the load on the blast furnace, and reduce the melting temperature of the chlorate slags, as suggested by some authors, is met by us with some reservations, as the activity of the hematite crystals will be imposed on any other criteria. The pyroconsolidation temperature would have to be limited to low temperatures to assure that the slag has a significant MgO content that would allow an increase in its melting point.

We can conclude that when MgO is present in appreciable quantities, it dissolves into the hematite crystals easily from the beginning of the experiment, and that, after that, as the temperature is raised, it encourages transformation of the crystals, resulting in the appearance of a certain amount of magnetite.



**Figure 13.** Behavior of MgO during pyroconsolidation.

The dissolving which takes place at the beginning of the experiment occurs through a solid–solid reaction, with the MgO spreading from its origin toward contiguous grains of hematite. It does this in such a way that even at the lowest temperatures used in the study, appreciable amounts of ferrous appear in the crystals. With the rise in temperature, MgO continues to spread to hematite crystals throughout the pellet, so that the number of crystals affected – and thus, the number undergoing the dissociation process – continues to grow. The grains of magnesite dissolve completely in the hematite crystals, including the MgO from the areas of slag, causing the amount of MgO in the slag to decrease. **Figure 13** shows the behavior of this compound.

Regarding the CaO, it is found primarily in calcium silicate slags, and a small quantity is found dissolved in the hematite grains. It does not, however, appreciably affect the dissociation. As in the case of pellet P6-6, CaO forms slag with a low melting point, providing a vehicle for the migration of MgO to the hematite grains.

#### 4. Conclusions

The analysis of the results obtained in this research lead us to the following conclusions:

- (1) The content of  $\text{Fe}^{2+}$  in pyroconsolidated pellets of magnetite oxide, at temperatures lower than expected from thermodynamic predictions is due to a premature dissociation process caused by MgO contained in additives or in gangue components.
- (2) The MgO dissolves in the hematite crystals forming a solid solution from the very beginning of the process, remaining in solution even though the hematite transforms into magnetite.
- (3) The content of  $\text{Fe}^{2+}$  in pyroconsolidated pellets increases with the alkalinity of the pellet. For a particular alkalinity, the  $\text{Fe}^{2+}$  content increases based on the MgO/CaO ratio.
- (4) When the MgO/CaO ratio is low and the alkalinity is medium or high, at the beginning of the pyroconsolidation process, limestone additive reacts with the hematites and calcium silicates from the gangue to form ferrites. Raising the temperature causes the ferrites to incorporate the calcium silicates, which at higher temperatures breaks down into new hematites and calcium silicates.
- (5) When CaO and MgO are added together, the MgO is the first compound to react with  $\text{SiO}_2$  to form silicates, leaving the CaO free to form ferrites, which later dissolve in the magnesium silicate formed, providing a vehicle for the migration of MgO to the hematite crystals.
- (6) At higher temperatures, around  $1150^\circ\text{C}$ , the MgO present causes the transformation of hematite into magnetite, the quantity depending on the concentration of MgO in the hematite crystals.

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**Keywords:** pellet; pyroconsolidation; magnetite; hematite; blast furnace

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