Study of the silica–magnesia relationship in silicate slags on electrical conductivity at high temperature

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Abstract. Slags are metallurgical aggregates with beneficial minerals and in some processes, they constitute the most abundant mass of the operation and for this reason their control is necessary. These materials have physicochemical behaviors that serve to model the process variables. A particular condition of silicate slags in processes for obtaining some ferroalloys is that there are relationships between compounds that allow predicting the behavior of other variables, these relationships are maintained during production. This study aims to know the electrical behavior of a slag so that the data will contribute to have an additional control in the operation of an electric arc furnace. An alumina content of up to 50% was gradually added to one sample and the other was remelted on three occasions, for all cases the electrical conductivity was determined at a temperature between 1400 °C and 1600 °C. For the electrical resistance value, a Miller 400 type resistivity measurement device was used, and the temperature was achieved by melting the samples in a high-frequency induction furnace with a collapsible silicon carbide crucible, lined with high-grade refractory alumina. Analysis of the electrical conductivity data for silicate slags made it possible to demonstrate that they are proportional to the values of the major oxides of the slag in their silica–magnesia ratio.

1. Introduction
In the world there are different ways of processing nickel lateritic minerals in order to obtain ferronickel, which in turn can be used as a base raw material that allows nickel to be delivered and thus obtain different types of alloys, internationally the highest alloy production from this ferroalloy is stainless steel. Mineral treatments require operations with large-volume movements, the above due to the fact that the ore nickel tenor varies from 1.5 to 2.5%, in a first phase a pre-reduction in a rotary furnace is done and then passes to an immense circular or rectangular electric arc furnace, where fusion is possible with the application of electrical energy on the order of 500 to 600 kWh [1] per ton during the process. The low grade requires a mass of at least 20 tons of material for the production of one ton of ferronickel with 35% nickel [2]. The above means that the electric arc furnace produces a slag metal ratio of 1 to 20, the slag under these conditions becomes the material to be controlled. Controlling the slag composition also modifies the internal operating conditions in the conductivity or ease with which the reactor can be maintained at the appropriate temperature that allows both the separation of the slag with the metal, and the evacuation of the slag that, due to its density of 3 g/cm³, super nates the metal film of density 8 g/cm³, each species is evacuated in different areas of the oven.

Accounting for the possibility that the composition of the slag is altered by some of the components, two experiments were developed, one modifying the alumina content from 5 to 50%, the object of this is to saturate this component and thus identifying its effect on extreme conditions. In a second
experiment, we took a slag sample and recast it three times, to find out the effects of fusion on both the composition and the electrical conductivity tests. The mechanism used to measure the conductivity consists of a resistance test with a Miller 400 soil resistivity advice, and based on literature, the conductivity values were used in a formula that takes into account the accessories that were used such as diameter and graphite electrode separation.

The results of the tests were validated with different software and bibliographic material [1] where conductivity values and chemical composition data can be correlated, which allows to present coherent results adjusted to the experience in industrial work and scientific developments whose objective is to know the electrical behavior of a slag in a reactor, where the main mass is slag with a predominant percentage of silica.

2. Materials and methods
The slag samples were obtained in the pilot plant of the Universidad Pedagógica y Tecnológica de Colombia, which consists of a rotary kiln with a capacity of up to 180 kg/h of lateritic mineral and an electric arc furnace to process up to 80 kg of calcine (material that passes through the rotary kiln where it is pre-reduced); the furnace electric uses about 909 kWh/ton of calcine. Once the calcine has been melted and cast in a metal mold protected with CO2 refractory sand, it is separated from the metal and the slag blocks are obtained, which after being cooled are mechanically prepared to a particle size of 2 mm. In Figure 1, the casting of a calcine melt on the metal container protected with CO2 molding sand is shown.

2.1. Slag melting
To melt the slag, a high-frequency induction furnace, a German-made model of the company VEM VEB Inducal Göttingen reference IMKW 02/8, with a nominal power of 40 kW and operating power of 28, is used as a reactor kW for 0.75 kV. Taking into account the need to place a ferromagnetic element in the furnace, a silicon carbide crucible is used and to avoid contamination a refractory layer approximately 4 mm thick is placed, which was made of a mixture of high alumina refractory concrax 1700 [2].

2.2. Electrical records
The electrical records were taken with the help of a Fluke 430 series II device, which analyzes the energy and quality of three-phase power and also records the energy losses caused by harmonics and the way in which the three-phase systems are distributed. The device is connected to each electrode through a flexible cable and in its configuration, it achieves the recording of each measurement, without one specific configuration [3].

2.3. Resistance measurement
To measure the resistance of the hot slag, various accessories are used inside the crucible, the graphite electrodes, the alumina thermowell, the platinum-rhodium thermocouple and the metal connectors protected with porcelain ceramics, see Figure 1. Resistivity is calculated from experimental resistance measurements (R in Ω) and with the use of the following Equation (1), proposed by Birol et al. [4].

\[ \rho = \frac{R \cdot \pi \cdot r (r+2h)}{l}, \]  

(1)

where r is the radius of the electrode, h is the depth of immersion of the electrodes, and l is the length or distance between electrodes, see Equation (1).

Electrical conductivity in (Ω cm)−1 is the inverse of electrical resistivity in (mΩ.m), as shown in Equation (2), see Equation (2), and is a measure of a materials ability to conduct an electric current [4].

\[ \kappa = \frac{1}{\rho}. \]  

(2)
3. Results and discussion

The chemical composition results were obtained for each of the slag samples, and also for the sample that was recast 3 times by x-ray fluorescence (XRF) test. The values are shown in Table 1 and Table 2.

Table 1. Slag chemical composition alumina mixtures.

| Mixture     | NiO  | FeO  | MgO  | SiO₂ | Al₂O₃ | SiO₂/MgO ratio |
|-------------|------|------|------|------|-------|----------------|
| 1 (0% Al₂O₃)| 0.15 | 28.29| 19.91| 47.15| 4.51  | 2.37           |
| 2 (5% Al₂O₃)| 0.14 | 26.84| 18.86| 44.72| 9.45  | 2.37           |
| 3 (10% Al₂O₃) | 0.14 | 25.39| 17.82| 42.29| 14.36 | 2.37           |
| 4 (20% Al₂O₃) | 0.11 | 22.53| 15.76| 37.47| 24.12 | 2.38           |
| 5 (30% Al₂O₃) | 0.10 | 19.69| 13.72| 32.71| 33.77 | 2.38           |
| 6 (40% Al₂O₃) | 0.08 | 16.89| 11.70| 28.00| 43.33 | 2.39           |
| 7 (50% Al₂O₃) | 0.07 | 14.11| 9.70 | 23.33| 52.79 | 2.41           |

Table 2. Slag chemical composition remelting.

| Melting | NiO  | FeO  | MgO  | SiO₂ | Al₂O₃ | SiO₂/MgO ratio |
|---------|------|------|------|------|-------|----------------|
| 1       | 1.52 | 24.55| 21.38| 48.09| 4.46  | 2.25           |
| 2       | 1.01 | 22.90| 19.54| 49.10| 5.21  | 2.51           |
| 3       | 0.39 | 20.51| 19.96| 52.93| 6.22  | 2.65           |

Table 1 and Table 2, present the values of the most important oxidized compounds of the slag, here the nickel losses in the slag are evident, a phenomenon associated with the operation of the furnace and the level of reduction that is reached in the previous stage of calcination [5], also the SiO₂/MgO ratio is maintained because the compound that is modified with the addition of alumina. Regarding the remelted...
slag, a progressive loss of the oxidized iron and nickel compounds is observed. This is due to the separation in the fusion of iron and nickel metal in the form of ferronickel. Regarding the other compounds, the ratio is increased by the loss of some MgO that is reduced the alumina increases but by dilution and is the most stable compound, followed by the silica. Regarding the current consumption, the Fluke 430 series II advice, gave the following general results of a typical fusion in the electric arc furnace.

Table 3. Average power consumption values for the 3 electrodes and the measured 3-phase power common to Fluke 430 Series II advice.

| Melting time | Power factor | Electrode current 1 | Electrode current 2 | Electrode current 3 | Electrode voltage 1-2 | Electrode voltage 2-3 | Electrode voltage 3-1 | Specific Consumption |
|--------------|--------------|---------------------|---------------------|---------------------|----------------------|----------------------|----------------------|---------------------|
| 45 Minutes   | 0.99         | 788 Amps            | 880 Amps            | 779 Amps            | 159 Volts            | 170 Volts            | 178 Volts            | 909 kWh/ton         |

The energy consumption values of 909 kWh/ton (Table 3) of calcine processed are very high compared to data from an industrial processes 550 kWh/ton of calcine, this is due to the smaller size of the pilot reactor and the uncontrolled energy losses in the electric arc ignition, connection and sustaining operations, the latter is hampered by the physical and electrical changes of the calcine charge when it melts to become slag and metal. The electrical resistance values were obtained at industrial operating temperatures between 1400 °C and 1600 °C. After applying Equation (1) and Equation (2), the electrical conductivity values were obtained for each slag sample and recorded in Table 4 and Table 5; the experimental resistance values decrease as the temperature increases, therefore the calculated conductivity behavior with regard to the temperature is directly proportional, which is in line with others previous investigations [6].

Table 4. Conductivity and electrical resistivity values calculated using experimental data of resistance at temperatures of interest for each of the slag remelting.

| Slag 2     | Temperature (°C) | Resistance (Ω) | Resistivity (mΩ.m) | Conductivity (Ω.cm)^-1 |
|------------|------------------|----------------|--------------------|------------------------|
| Melting 1  | 1400             | 2.60           | 65.45              | 0.15                   |
|            | 1500             | 1.90           | 47.83              | 0.21                   |
|            | 1550             | 1.55           | 39.02              | 0.26                   |
|            | 1600             | 1.10           | 27.69              | 0.36                   |
| Melting 2  | 1400             | 2.60           | 65.45              | 0.15                   |
|            | 1500             | 2.15           | 54.12              | 0.18                   |
|            | 1550             | 1.90           | 47.83              | 0.21                   |
|            | 1600             | 1.70           | 42.79              | 0.23                   |
| Melting 3  | 1400             | 4.90           | 123.35             | 0.08                   |
|            | 1500             | 3.80           | 95.66              | 0.10                   |
|            | 1550             | 3.25           | 81.81              | 0.12                   |
|            | 1600             | 2.70           | 67.97              | 0.15                   |

Figure 2 shows the generalized behavior between the mixtures corresponding to slag 1 and the respective melts of slag 2 where the electrical conductivity in both cases decreases as the SiO₂/MgO ratio increases, a trend that is maintained for all temperatures. In Figure 2(a), where, the electrical conductivity results calculated in Table 5, were plotted against the SiO₂/MgO ratio values of Table 1, the addition of alumina caused a pronounced drop in electrical conductivity from mixture 1 with 4.3% Al₂O₃ within its chemical composition to mixture 3 with 10% added alumina and where this still has a silicate slag typical of the ferronickel production process given the predominance of the major species...
SiO$_2$, MgO and FeO (Table 1), as the unusual content of alumina of mixture 4 with 20% increases to mixture 7 with 50%, the partial formation of an alumina matrix is theoretically assumed that begins to predominate over the silicates of the slag, defining its electrical behavior, giving a stabilization tendency to the drop in the conductivity. In Figure 2(b), where, the electrical conductivity results calculated in Table 4, were plotted against the SiO$_2$/MgO ratio values of Table 2, associated with the increase in the SiO$_2$/MgO ratio and the loss of Fe and Ni due to the re-fusion of the sample, a small decrease in electrical conductivity is observed, with fusion 1 being the one that presented the highest conductivity 0.36 S/cm at 1600 °C; in relation to fusion 2 and fusion 3 where the lowest conductivity was observed 0.23; 0.15 S/cm respectively at the same temperature, note that the same trend is maintained independent of the temperature analysis.

Previous research has shown that the electrical conductivity of the slag comes from ions that can be mobilized under the electric field, forming a three-dimensional network structure where basic oxides can break the network structure of acidic oxides, favoring the transport of electric charges given the release of oxygen ions [7-9]. Therefore, in Figure 2(b), as the content of basic oxides, especially FeO and NiO, are partially reduced, attributed to the loss of metal in each melt (Table 2), in parallel and because of such reduction, the content of acidic oxides such as SiO$_2$ is enriched, bringing with it an increase in the SiO$_2$/MgO ratio, with 2.25 for fusion 1 and 2.51 and 2.65 respectively for fusion 2 and 3, inversely proportional to this the conductivity decreases.

Table 5. Conductivity and electrical resistivity values calculated using experimental data of resistance at temperatures of interest for each of the slag alumina mixture.

| Slag 1 | Temperature (ºC) | Resistance (Ω) | Resistivity (mΩ.m) | Conductivity (Ω.cm) |
|--------|-----------------|----------------|--------------------|---------------------|
| Mixture 1 | 1400           | 1.57           | 39.52              | 0.25                |
|         | 1500           | 0.96           | 24.17              | 0.41                |
|         | 1550           | 0.83           | 20.89              | 0.48                |
|         | 1600           | 0.70           | 17.62              | 0.57                |
| Mixture 2 | 1400           | 2.60           | 65.45              | 0.15                |
|         | 1500           | 1.81           | 45.56              | 0.22                |
|         | 1550           | 1.70           | 42.79              | 0.23                |
|         | 1600           | 1.60           | 40.28              | 0.25                |
| Mixture 3 | 1400           | 3.34           | 84.08              | 0.12                |
|         | 1500           | 3.12           | 78.54              | 0.13                |
|         | 1550           | 3.01           | 75.77              | 0.13                |
|         | 1600           | 2.90           | 73.00              | 0.14                |
| Mixture 4 | 1400           | 4.40           | 110.76             | 0.09                |
|         | 1500           | 4.10           | 103.21             | 0.10                |
|         | 1550           | 3.95           | 99.43              | 0.10                |
|         | 1600           | 3.80           | 95.66              | 0.11                |
| Mixture 5 | 1400           | 6.82           | 171.68             | 0.06                |
|         | 1500           | 5.91           | 148.77             | 0.07                |
|         | 1550           | 5.56           | 139.96             | 0.07                |
|         | 1600           | 5.20           | 130.90             | 0.08                |
| Mixture 6 | 1400           | 9.30           | 234.11             | 0.04                |
|         | 1500           | 9.10           | 229.07             | 0.04                |
|         | 1550           | 7.80           | 196.35             | 0.05                |
|         | 1600           | 7.60           | 191.31             | 0.05                |
| Mixture 7 | 1400           | 10.70          | 269.35             | 0.04                |
|         | 1500           | 10.30          | 259.28             | 0.04                |
|         | 1550           | 10.10          | 254.25             | 0.04                |
|         | 1600           | 9.90           | 249.21             | 0.04                |
According to Mills [10,11], Al$_2$O$_3$ in liquid state is trivalent, being in ionic form (Al$^{3+}$) forming ionic oxides of alumina such as AlO$_4^{-}$ among others, which due to their amphoteric nature are exhibited as acidic oxides under conditions of low basicity acting as ionic network formers that obstruct the circulation of electric charges and in conditions of high basicity they act as basic oxides with the ability to modify ionic networks which in turn allows the movement of electric charges [12]. Under this criterion the behavior of Figure 2(a), is justified where mixture 1, which represents the initial composition of the sample, contains 4.51% Al$_2$O$_3$ and a SiO$_2$/MgO ratio of 2.37 records the highest conductivity among all the mixes and each of the analysis temperatures, in turn, as soon as 5% by weight of alumina is added, the conductivity decreases drastically while the relationship remains almost stable, a tendency that extends until mixture 3, with 14.36% Al$_2$O$_3$ and a SiO$_2$/MgO ratio of 2.37. It should be noted that up to this point, real percentages of alumina are still preserved in industrial practice, now continuing with the saturation of the compound from mixture 4 with 24.12% Al$_2$O$_3$ and 20% added by weight, the conductivity decreases moderately to the 40% corresponding to mixture 6 where the predominance of alumina over the silicates and basic oxides of the slag is already noticeable, maintaining the increase in the SiO$_2$/MgO ratio in an almost constant state (Table 1), once the alumina content exceeds 50% of the total species in mix 7, and taking into account the experimental operating parameters, the point of maximum concentration is reached, which generates a stable trend of electrical conductivity at each of the analysis temperatures. Conductivity is directly proportional to temperature.

![Figure 2. Behavior of electrical conductivity with respect to the SiO$_2$/MgO ratio at temperatures between 1400 ºC and 1600 ºC: (a) corresponding to the additions of alumina, (b) corresponding to the re-melting of the same sample.](image)

4. Conclusions

Thanks to the analysis carried out in this work, it was possible to achieve an important understanding of the effect on the electrical conductivity and chemical composition that a species causes within a typical silicate slag during the process of obtaining ferronickel, allowing us to know how the electrical behavior would be modified, due to the increase in alumina in this case. Also, this mechanism to predict operating and design conditions will allow better decisions to be made in the improvement and control of the electrical variables of the reactor. The FeO contents are not solely responsible for the conductivity, the SiO$_2$/MgO ratio has a direct effect on the electrical behavior of the slag. It is necessary to take into account that all oxides affect electrical conductivity differently, and that this is responsible for the heating of the calcine charge in the reactor and its conversion into liquid slag; the aforementioned allows control decisions and operation with a higher composition-power supply ratio.
In the operation model of the electric arc furnace, when the electrical conductivity of the slag decreases due to high percentages of Al2O3, the resistance to the passage of electrons consequently increases, this produces a positive effect because a greater resistance to the current passing the calcine particles that form slag at the tip of the electrodes will increase the heating rate and hence the melting rate.

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