

## Chemical and mineralogical characterization of silicon manganese iron slag as railway ballast

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### Abstract

In nature, metal ores such as iron, lead, aluminum and others are found in an impure state, sometimes oxidized and mixed with silicates of other metals. During casting, when the ore is exposed to high temperatures, these impurities are separated from the molten metal and can be removed. The mass formed by these compounds is slag. Slag is the co-product of the smelting of ore to purify metals. It may be considered a mixture of metal oxides, but may also contain metal sulphites and metal atoms in their elemental form. After it is reprocessed to separate the metals contained, the co-products of this process can be used in cement, rail ballast, road paving and various other purposes. The objective of this research work is the presentation of the chemical and mineralogical characterization tests of the silicon-manganese iron slag with the purpose of reusing the co-product as rail ballast. X-ray diffraction tests, quantitative chemical analyzes, scanning electron microscopy and free lime content were prepared for these characterizations. The results of these tests showed the technical feasibility of using slag as rail ballast.

**Keywords:** alternative ballast; Silicon-Manganese Iron Slag (FeSiMn); environmental characterization and classification.

## 1. Introduction

Ferroalloys are essential inputs in the steel industry, as they are indispensable in the manufacture of all types of steel, both in the basic processes and in the refined property and value aggregation in special steels (Andrade *et al.*, 1999). Basically the most conventional ferroalloys are ferro-silicon, ferrochromium, ferro-silicon-manganese and ferromanganese, and are present in almost all the processes of iron and common or special steel production.

Among the types of alloys, the most prominent in their production are the manganese alloys. They are applied in the manufacture of virtually all types of steel and iron castings due to their desulfurizing and deoxidizing properties (Andrade and Cunha, 2000).

The production process of the silicon-manganese iron alloys (FeSiMn) consists of

the simultaneous reduction of manganese and silicon by carbon in electric reduction furnaces (FER). The charges consist of manganese ore and quartz (or quartzite) or manganese ore, rich slag and quartz (or quartzite). These charges are complemented by fluxes and reducers, which are used to adjust the composition of the steel co-product (slag) in the process.

According to Olsen and Tangstad (2004), the distribution of Si between SiMn alloys and multicomponent MnO-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>-MgO slags is mainly determined by the process temperature. The silicon content from silica will increase by approximately 6 % per 50 °C in the temperature range from 1550 °C to 1700 °C. This process is only feasible if the reduction temperatures of both oxides are close to each other. An-

other aspect to consider is the melting point of the slag: if it is below the silica reduction temperature, the furnace will continuously spend energy in melting, to the detriment of the reduction reaction.

Thus, two basic procedures are required in the formation of slag. The first one contemplates the reduction of the MnO activity (lower basicities of the slag) to increase the temperature of reduction of the manganese approaching the silicon reduction temperature. In the second, the formation of the slag with higher melting points compatible with the process temperatures can be obtained. This is done by acting on the charge formulation. One of the most relevant aspects of the process is the distribution of Si and Mn between the Mn-Fe-Si-Cs at alloys and the slag of the MnO-SiO<sub>2</sub>-CaO-MgO-Al<sub>2</sub>O<sub>3</sub>

system. The equilibrium relationships between the two systems for the Carbon

Monoxide (PCO) pressure equal to 1 atm are shown in Figure 1, which shows the

diagram of the system considered (Ding and Olsen, 2000).

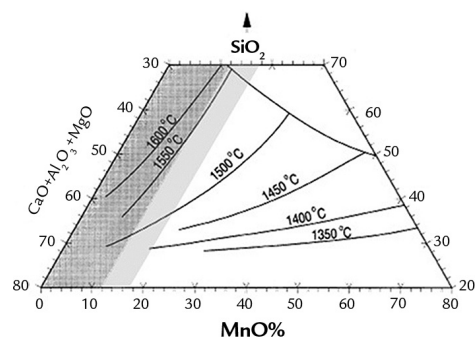


Figure 1  
Diagram of metal-slag-gas equilibrium (Ding and Olsen, 2000).

There are several proposed equilibrium relationships for these systems. Each refers to existing conditions, whether in statistical data of one or several installations, or in specific experiments.

There are two types of slag formed by the described production processes: the

rich slag, which is acidic, presents high Mn contents (above 40 %), being recyclable and reused as an input in FeSiMn production (besides having very low phosphorus content, which is an advantage for the FeSiMn production), and poor basic slag, which has low manganese content (MnO < 20 %) and

about 30 % of Si is produced by upgrading the standard alloy through addition of silicon waste from the iron silicon industry, which at the end of the ferroalloy production process, is discarded (Olsen and Tangstad, 2004). Figure 2 shows the silicon iron manganese slag.

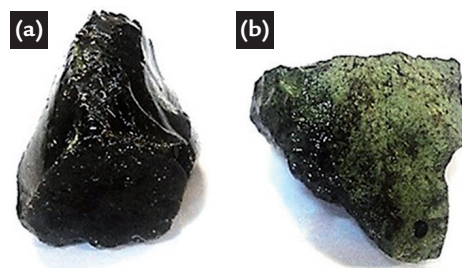


Figure 2  
Silicon-manganese iron slag (a) rich and (b) poor.

The use of slag as a base material for pavement layers and as a rail ballast has been

researched by other authors, Silva (1991); Kandhal and Hoffman (1998); Bagampadde

*et al.* (1999); Rohde (2002); Fernandes (2005); Nóbrega (2007); Fernandes (2010) and others.

## 2. Materials and methods

As mentioned earlier, there are two types of slag formed by the described production processes: rich and poor slag. The rich slag is acidic, because it contains high levels of Mn, undergoes vitrification that decreases its resistance and makes it dangerous for handling. This high content of Mn contained in the rich slag is reused as an input in FeSiMn production. Thus, because it is a basic co-product with low manganese content, has a resistance greater than that of the rich slag and is

not being reused in the production of FeSiMn, the silicon-manganese iron slag used for this study was the basic (poor) slag. For that, slag samples provided by a silicon-manganese iron producer in Minas Gerais, at its Ouro Preto-MG unit, were used, which has a production capacity of 5000 t / month, with 3000 t / month of material processed for use as a rail ballast. The sample of the material was initially subjected to X-ray diffraction, quantitative chemical analyses, scanning electron

microscopy and free lime content assay.

For the accomplishment of these tests the material was submitted to the granulometric reduction process. It was then sieved, where approximately 20 kg of the sample passed through a sieve of either 200 or 75  $\mu\text{m}$ . All the tests have as reference the standards established by ABNT (Brazilian Association of Technical Standards), AREMA (American Railway Engineering and Maintenance Association).

### X-Ray Diffraction Analysis

A Shimadzu diffractometer, model D / MAXB, with iron tube and scanning range of 7° to 70° and radiation of 20 kV and 5  $\mu\text{A}$  was used in the analysis. The speed adopted in the test was 2 degrees / minute lasting  $\pm$  35 minutes.

The analysis of the results is processed through specific software (MDJ Jades), which compares the peak of the incidence of electrons with a database available for the characterization of the constituent minerals.

$$n\lambda = 2d\sin\theta$$

Being: n - integer known as the order of the diffracted beam;  $\lambda$  - wavelength of the

apparatus tube;  $\theta$  - incidence angle and d - interplanar distance (spacing).

The records of this optical process are collected in a detector in the form of an amplified electrical signal, which is recorded in digital or analog form, cor-

responding to the diffractograms. The diffractograms present characteristic peaks that are the results of X-ray diffraction in crystallographic planes of the sample,

related to the position, intensity and shape of the crystalline structure, thus characterizing the mineralogical composition of the analyzed materials.

### Quantitative chemical analysis

It is by measuring the intensity of the characteristic X-rays emitted by the sample's elements that the quantitative analysis by X-ray fluorescence is based on. A radioactive source emits X-rays, which excite the constituent elements and, in turn, emit spectral lines with characteristic energies of the element and whose intensities are related to the concentration of the element in the sample. X-ray fluorescence analysis consists of three phases: excitation of the sample elements, dispersion of the characteristic X-rays emitted by the sample and detection of these X-rays emitted. The X-ray fluorescence spec-

trometer is an instrument that enables the quantitative determination of the elements present in a given sample by applying X-rays to the surface of the sample and the subsequent analysis of the fluorescent rays emitted.

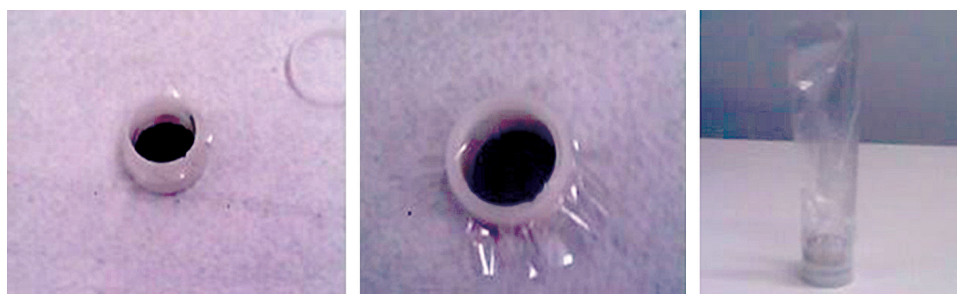
In the analysis, a Shimadzu Energy Dispersion X-ray spectrometer, model EDX-700 HS / 800 HS / 900 HS was used. The samples used in this experiment went through two types of preparation: The first preparation was carried out with 20 g of pulverized sample passed through the 75 µm sieve. Then the sample was heated between 100 °C and 120 °C in the furnace, after which

0.6 g of estuary acid -  $C_{18}H_{36}O_2$  (acts as a 'glue' to fix the sample) were added. Next, the sample was further sprayed for 4 minutes to mix the sample material with the estuary acid, and then the mixture was pressed into the pallet form. In the second preparation, 10 g of pulverized sample was passed through the 75 µm sieve, and then the sample was placed in a plastic ring sealed by a plastic filter and inserted into another plastic bag with the tips cut to form a vacuum in the sample for the test. Samples prepared for the X-ray fluorescence assay are shown in Figures 3 and 4 for the first and second assemblies.

Figure 3  
Samples prepared in the first assembly for the assay.



Figure 4  
Samples prepared in the second assembly for the assay.



### Chemical analysis by scanning electron microscopy

For the observation and distinction of different types of minerals stemming from the emission and interaction of electron beams on a sample, the Scanning Electron Microscopy technique was used, which allows the characterization from the point of view of its morphology, its organization and its chemical composition. What is observed in the scanning electron microscope is due to the contrast variation, which occurs when a primary electron beam sweeps the surface of the sample in point-to-point analysis. The

qualitative distinction of the particle morphology of the samples of the study materials was made using an electronic scanning electron microscope of the JEOLJSM-5510 type.

In the test, the samples need to be conductive in the presence of carbon and, for this, they undergo the metalization process. The samples are thus arranged in the form of monolayers in metal cylindrical pieces (pallets), coated with graphite by a double-sided tape, then deposited in a vacuum evaporator for a period of about 1 hour. The

graphite electrodes are then vaporized for about 10 minutes. After this process, the sample becomes conductive and the pallet is introduced into the chamber of the microscope, making a vacuum of 3 minutes. The samples are subjected to electron bombardment processes, and then photomicrographs are made. In this study, the adopted increases were 50x, 100x, 150x to 270x in the samples, using different accessories such as X-ray spectrometers, retro-scattered electron detector, absorbed electron detector, and transmitted electron detector.



### Free lime content

In determining the free lime content, the test method prescribed by NBR NM 13/2004 - Portland Cement - Determination of free calcium oxide by ethylene glycol (ABNT) was used as reference. This standard specifies the determination of free calcium oxide by dissolution in ethylene glycol and subsequent titration in standard solution of hydrochloric acid (HCl) using

a mixture as a pH indicator (mixed indicator solution).

For the assay, three samples containing 1.00 g each were weighed and mixed in three capped Erlenmeyer flasks, each containing 30 ml of corrected (green) pH ethylene glycol. The flasks were then heated in a water bath at 65 °C to 70 °C for 30 min, shaking the flask every 5 minutes.

$$\text{CaO}_{\text{free}} = \frac{F \times V \times 0.002804}{m}$$

Where, F - HCl Factor; M - Mass of crushed sample employed in the test; V - Volume of HCl used in the titration.

This method does not differentiate oxide [Ca (OH)] from hydroxide [Ca (OH)<sub>2</sub>] and does not determine the calcium that is chemically combined in solid solution with FeO and MnO or in

the form of silicates. However, in the scope of the analyses intended in this study, the results of this test are more than satisfactory. They serve as a basis for estimating the percentage of free

lime, which causes the expansion that is responsible for causing the spontaneous breaking of the grains, which in turn causes the excess of fines that is harmful to the ballast.

### 3. Results of tests and discussion

Since there is no specific technical standard for silicon-manganese iron slag both in Brazil and abroad, the values found in the analyzes were compared

with the indexes recommended by AREMA (2001) for LD steel mill slag. In order to use the LD steel mill slag ballast, it must have a percentage of cal-

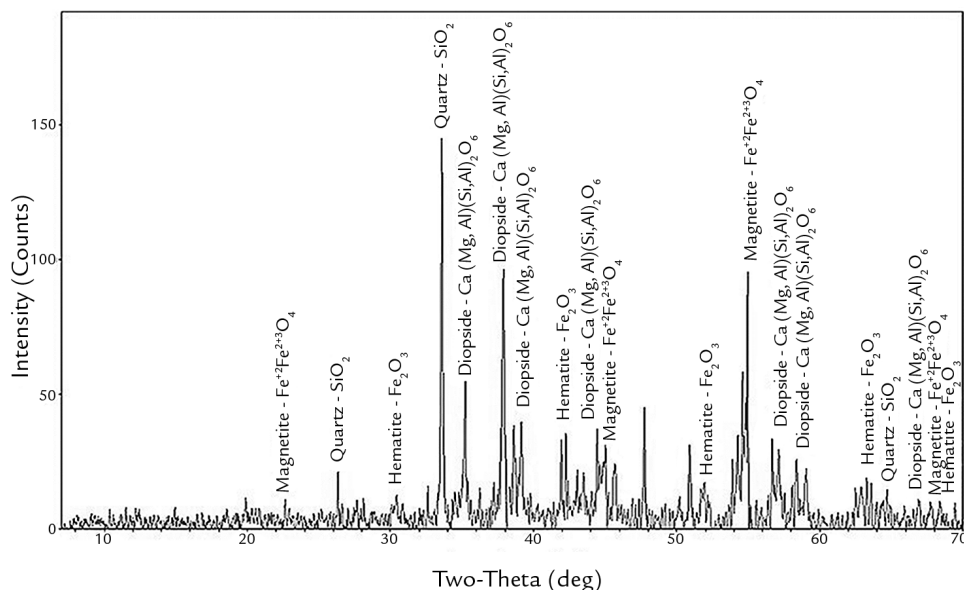
cium oxide (CaO) of less than 45 % and a sum of aluminum oxides (Al<sub>2</sub>O<sub>3</sub>) and iron (Fe<sub>2</sub>O<sub>3</sub> and FeO) of less than 30 % (AREMA, 2001).

### X-Ray Diffraction Analysis

The X-ray diffraction patterns of the silicon-manganese iron slag show

the mineralogical phases of the material. Figure 5 shows the X-ray diffrac-

tion patterns of the silicon-manganese iron slag.



The predominant mineralogical constituents found in the silicon-manganese iron slag sample are: Magnetite-

Fe<sup>2+</sup> Fe<sup>3+</sup>O<sub>4</sub> (iron and oxide); Quartz - SiO<sub>2</sub> (silicon and oxide); Diopside - Ca (Mg, Al) (Si, Al)<sub>2</sub>O<sub>6</sub> (calcium, manga-

nese, aluminum, silicon and oxide); Hematite - Fe<sub>2</sub>O<sub>3</sub> (iron and oxide).

### Quantitative Chemical Analysis

For this first preparation, the pure chemical species were analyzed. Table

1 shows the pure chemical species in percentage.

Figure 5  
X-ray diffraction patterns of slag.

Table 1  
Pure chemical species  
and their percentage by  
mass of the first preparation.

Chemical species (% by mass)												
Material	Si	Mn	Al	Ca	Fe	K	S	Tb	Ba	Sr	Cr	Zr
Slag	38.594	21.277	16.131	14.680	5.541	2.299	0.446	0.442	0.387	0.109	0.077	0.017

For the second preparation, the composite chemical species were analyzed.

Table 2 presents composite chemical species and their percentage.

Table 2  
Composite chemical species  
and their percentage by mass  
of the second preparation.

Chemical species (% by mass)										
Material	SiO <sub>2</sub>	MnO	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	SO <sub>3</sub>	Tb <sub>4</sub> O <sub>7</sub>	BaO	SrO
Slag	14.490	45.946	8.417	11.558	9.663	8.389	0.133	1.123	0.000	0.281

The chemical analysis of silicon-manganese iron slag showed that the highest percentage of calcium oxide

(CaO) found was 11.558 %, and the sum of aluminum oxides (Al<sub>2</sub>O<sub>3</sub>) and iron (Fe<sub>2</sub>O<sub>3</sub>) was 18.080 %, proving that

the results were below the values recommended by AREMA (2001).

### Chemical analysis by scanning electron microscopy

Semi-quantitative chemical analysis was performed on the pulverized material. Table 3 systematizes the com-

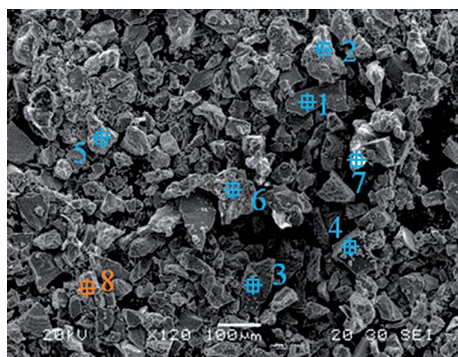
posite chemical species found and their respective percentages for each point of analysis. Figure 6 shows the morpho-

logical distribution obtained in the slag powder analyses.

Table 3  
Composite chemical species  
and their percentage by mass.

Chemical species (% by mass)								
Points	CO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	MnO	Fe <sub>2</sub> O <sub>3</sub>
1	50.56	2.79	6.07	22.14	1.11	5.30	12.03	
2	61.82		7.99	12.40	1.35	1.79	10.63	4.03
3	61.74	1.49	6.47	17.56	1.33	5.23	6.18	
4	36.05			63.95				
5		4.69	15.88	31.00		31.74	16.70	
6	30.01	1.61	1.69	6.55	1.60	5.31	53.23	
7			10.05	26.07	4.52	16.54	42.81	
8				12.01		14.76	73.23	

Figure 6  
Typical morphology  
found in pulverized slag.



At the analyzed points, the carbon oxide, silicon oxide, calcium oxide and manganese oxide contents presented higher percentages, whereas carbon

oxide presented the highest percentage among all elements. The analysis of the slag showed that point 5 presented the highest values of calcium oxide (31.74 %),

and sum of aluminum and iron oxides (15.88 %), proving that the results found were below the values recommended by AREMA (2001).

### Free lime content

In determining the free lime content, the test method prescribed by NBR NM

13/2004 - Portland Cement - Determination of free calcium oxide by ethylene glycol

was used as a reference. Figure 7 shows the percent free lime content graph.

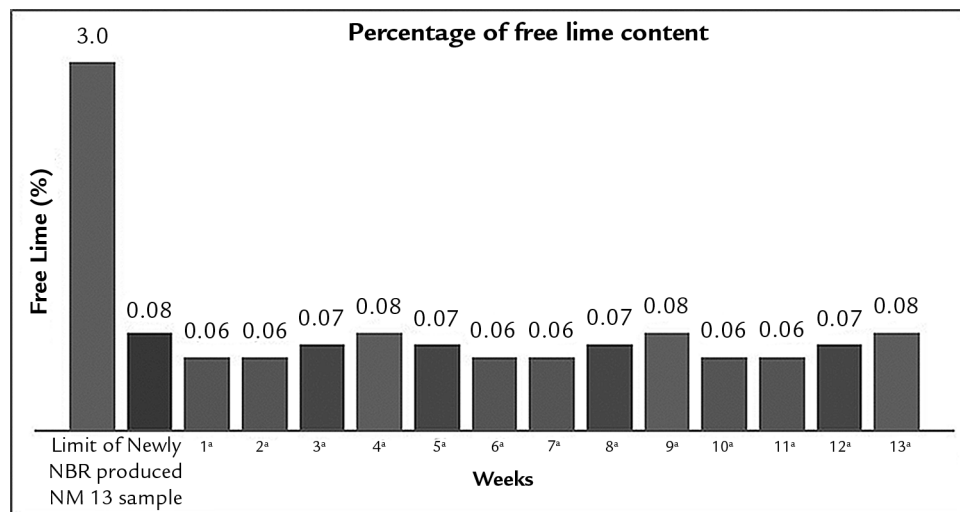


Figure 7  
Percentage graph of  
free lime content of slag.

The silicon-manganese iron slag presented a total mean of 0.07 % free

lime in a total of 13 trials in 13 weeks. The results show that the percentages

of free lime found in the slag are practically zero.

#### 4. Conclusion

The X-ray diffraction test showed that the sample has a mineralogical composition of magnetite, quartz, diopside and hematite.

The chemical analysis of silicon-manganese iron slag showed that the highest percentage of calcium oxide (CaO) and the sum of the aluminum oxides ( $\text{Al}_2\text{O}_3$ ) and iron ( $\text{Fe}_2\text{O}_3$ ) found were below the values recommended by AREMA (2001), that is, the sample complies with calcium oxide (CaO) limits of less than 45 % and a sum of less than 30 % of aluminum ( $\text{Al}_2\text{O}_3$ ) and

iron ( $\text{Fe}_2\text{O}_3$  and FeO) oxides prescribed by the standard.

In the scanning electron microscopy test, the analyzed points that presented, on average, higher percentages were the contents of carbon oxide, silicon oxide, calcium oxide and manganese oxide, with carbon oxide presenting the highest percentage of all the elements. The values found proved that the oxides found were below the maximum values recommended by AREMA (2001).

The free lime content test showed that

silicon-manganese iron slag presented a free lime mean total percentage of approximately zero, proving that the amount of lime in existence is well below the maximum limit recommended by the norm, which attests the inexistence of volumetric expansion.

In the steel production process, silicon-manganese iron slag has, among other things, the content of iron and calcium oxides, whose values are acceptable and therefore suitable to be used as railroad ballast, replacing the increasingly scarce and expensive natural materials.

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