Edited by Shadia Jamil Ikhmayies Bowen Li John S. Carpenter Jiann-Yang Hwang Sergio Neves Monteiro Jian Li Donato Firrao Mingming Zhang Zhiwei Peng Juan P. Escobedo-Diaz Chenguang Bai







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The Characterization of the Desulfurization Powder in the Semi-Dry De-SO <sub>2</sub> Process of the Sintering Plant Exhaust Gas and Its Interaction with the Soil Particles
Direct Synthesis of Carbon Nanotubes at Low Temperature by the Reaction of CCl <sub>4</sub> and Ferrocene
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Edited by: Shadia Jamil Ikhmayies, Bowen Li, John S. Carpenter, Jiann-Yang Hwang, Sergio Neves Monteiro, Jian Li, Donato Firrao, Mingming Zhang, Zhiwei Peng, Juan P. Escobedo-Diaz, and Chenguang Bai TMS (The Minerals, Metals & Materials Society), 2016

### CHARACTERIZATION OF WASTE MOLDING SANDS, FOR THEIR POSSIBLE USE AS BUILDING MATERIAL

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### Abstract

It was done a physicochemical and mineralogical characterization of the molding sand wastes of the iron casting process, being these sands the main residue of the process, representing 65 to 85 % of the total waste. According with the obtained results, the chemical composition of the material (expressed in weight percentages) is the following: 77.9 SiO<sub>2</sub>, 6.6 Al<sub>2</sub>O<sub>3</sub>, 8.56 Fe<sub>2</sub>O<sub>3</sub>, 0.14 TiO<sub>2</sub>, 2.48 MgO, 0.34 K<sub>2</sub>O, 1.52 CaO and 1.03 Na<sub>2</sub>O. The major mineral phases found were: Albite, Orthoclase, Quartz (anorthic) and Laihunite, and as minority phases were present both the Berlinite and the Montmorillonite. Furthermore the material presented a thick granulometry, around 60% corresponds to a particle size of  $53\mu$ m. According to this characterization, these residues could be used in the manufacture of construction materials such as bricks, blocks, or as a cementing material.

### Keywords

Molding sand waste, sustainability, steel industry.

#### Introduction

The technological development of recent decades has caused collaterally various environmental problems that have cost too much for society, as many ecosystems are reaching the limits of their capacity to assimilate wastes, resulting from the consumption of the population. It is in this way, that the functionality and comfort of the advancement of technology, based on the consumption of renewable and non-renewable natural resources, has put humanity at a crossroads: continue the culture of consumerism and disposability, thus forgetting the preservation of life on planet Earth, or commit to stop and reverse the effects caused to the environment due to technological "maturity".

The magnitude of the metallurgical industry worldwide, particularly in the steel industry, involves the problem of waste disposal of different processes that is of great importance, given the large number of them and due also to heavy mineral contents with differences in their composition [1].

Therefore, any waste disposal process that seeks its inerting involves considerable expense, so that strategies for treating these materials have experienced an evolution that seeks its transformation or reuse, to help reduce the costs of processing, compensating or in the best cases, to produce a benefit, that is, to reuse them in a new industrial process [2].

The main waste generated by the steel making activity, is the molding sand used in casting of ferrous and nonferrous metals. These are solid wastes with very low moisture content; the generation of this type of waste has increased in recent years in direct proportion to the advancement of technology in industrial production, and coupled with this, we can mention other factors such as increased consumption by the population, obsolescence of production equipment and improvements in technology, more and better productivity, and low cost of landfills in developing countries [2].

Currently the foundries located in the municipality of "Tepeapulco, Hidalgo" operate with about 3500 tons of recycled sand which is mixed daily with 20 tons of new sand, that is 99.94% of the used sand is recycled to same process and only 0.06% is discarded. These wastes (burnt silica sand) correspond to the portion of sand that was exposed to stresses and thermal effects, due it was in contact with the molten metal into molds and was reused an average of seven cycles, therefore it presents grains fractured, some debris (chips and scrap), burnt materials, and slag binders burnt. The above represents a total of 600 tons per month of wastes of molding sand.

In a study conducted in the UAEH [2], was obtained the characterization of the wastes of molding sand from the iron smelting process, in the zone of "Ciudad Sahágun"; the material characterized presented the following chemical composition expressed in percentages by weight of 70.1 % of SiO<sub>2</sub>, 14.7 % of Al<sub>2</sub>O<sub>3</sub>, 4.4 % of Fe, 0.20 % of MnO, 4.30 % of MgO, 0.40 % of K<sub>2</sub>O, 0.6 % of CaO and 5.26 % of Na<sub>2</sub>O. The above data show a type-bentonite composition, similar to that used in the original process, which let note that these residues could be used to manufacture building material such as blocks or bricks.

Therefore, treatment and reuse of these kind of wastes is proposed to allow a major contribution to mitigating environmental impact, generated due to the method of disposal of such waste, which basically consists of open dumps [3].

From the metallurgical point of view, are essential the corresponding characterization and leaching studies, to determine the feasibility of a revaluation of these wastes because they can be an alternative of use like raw material in other industrial processes, mainly for its adequate content of oxides of silicon, iron, aluminium, sodium and potassium, and their mineralogy as well as the distribution of chemical elements in their primary and secondary phases [4,5].

Also, it is important to have in account the possibility of that this residue could be a potentially pozzolanic material, because according to Montaño Cisneros *et al.*, it is necessary to have a percentage in the sum of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> of at least 70% [6]. According to the standard ASTM C618, a pozzolanic material needs a percentage in sum of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> of at least 70%, and a maximum percentage of SO<sub>3</sub> of 5%, for being considered as a material with high pozzolanic potential [7].

### Experimental procedure

For sampling, was necessary to consider the mineralogical and physical characteristics of the residual sand, so this was carried out systematically on different mounds of the sand bank, to cover the three dimensions of the mound where sampling was conducted (x, y, z), and was a type channel sampling, with a weight of 5 kilos each sample. Taking in account a length of 2 m by 0.30 cm. of wide, taking a total of 20 representative samples.

For characterization, the quartering of samples to know the material properties was performed, and was made a composite taking into account the similarity of the samples of each mound of sand, and the study was done by the following methods: X-ray diffraction, with an INEL diffractometer, model EQUINOX 2000, and for this analysis was necessary to prepare the sample to a -200 +270 mesh size (74-53 microns) then indexing of the results was done using the MATCH software version 1.10 [8]

The characterization by scanning electron microscopy, in conjunction with the microanalysis of energy dispersive spectrometry of x-rays (SEM-EDS) was used for the study of morphology of the particles, and microanalysis study was in order to determine the nature of the material studied. A SEM, brand JEOL, Model JSM 6300 equipped with a EDS detector of the brand Noran was used. The sieve analysis was performed on wet and this analysis was conducted with standard sieves (TYLER® series), No. 80, 100, 140, 200, 270, 400. Was sieved a sample of 100 g where the fractions obtained were dried at room temperature and then were subsequently weighed for its statistical analysis.

The residual molding sand from "Ciudad Sahágun" also was characterized through X-ray fluorescence, using a spectrometer Venus brand, model 200 MINILAB and the samples were prepared according to the following process:

Calcination of the material was performed previously, putting the sample into a porcelain crucible then heated in an oven at 800 ° C for 20 minutes, holding heating at this temperature, and then the sample was removed from the oven and was cooled up to 25 °C. Subsequently was prepared a pill for its use by FRX, for which 9 grams of LiB4 as flux and 0.9 grams of residual molding sand were used in a crucible of Au-Pt heated during 10 minutes in a Fluxy, until melting of the sample and its subsequently solidification at 25 °C, then it was characterized in the XRF spectrometer using a mixture of cooling gases with a composition of 90% Ar and 10% CH4, within the spectrometer.

### **Results and discussion**

The average chemical composition of residual sand from "Tepeapulco, Hidalgo", that was found by XRF, is shown in Table 1, where it is seen as major compounds to the silica, alumina and the iron oxide. The above, it allows us to say that this material basically is composed by silica sand with clay and slag, as impurities. The presence of  $ZrO_2$  may be due to that this compound was used for internal coating of the sand mold, before being filling with molten metal.

Element	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>
%	0.00	0.43	2.32	92.83	0.27	0.36	0.25	3.14	0.43

Table 1. Average chemical composition of the waste of sand, obtained by XRF.

The results of the average particle size analysis of the wastes, are shown in Figure 1 wherein it can be seen that the particle size is predominantly in the mesh 80 (177 microns) and has an average size of mesh 200 (74 microns), also showing that the greater weight is retained on the mesh 100 with a 19.18%, thereafter presenting, a very sharp drop to the mesh 400 (37 microns), where the minimum weight retained is of 4.50%. According to sieve analysis, it was determined that the material has a size that is within the specifications for its direct use in the manufacture of building materials and ceramic industry. The wastes of molding sand, can substitute to the fine and medium size sand for concrete building materials. In ceramic industry, the wastes of molding sand can be used with a small grinding, to achieve a particle size nearly of the mesh 200 (74 microns), or even lower sizes.



Figure 1. Particle size distribution of the wastes of molding sand

According to the phases obtained by X-ray diffraction (Figure 2), the major mineral phases were: Orthoclase,

Albite, Quartz Anorthic, Laihunite and Berlinite; these phases come from the same silica sand, as in the case of quartz, in addition to residual slag or the clay, that were formed by the weathering; like in the case of the majority of the rest of the phases present. As minor phase is present the Berlinite, and the residual phase is the Montmorillonite. The Berlinite was formed within the slag and also it was found a residual amount of Montmorillonite that was used to unite silica sand in the production of casting molds, during the green sand process. The total amount of Montmorillonite stops being of importance, because this phase is present in a lower concentration for a correct use in the green molding process, and it has a particle size less than to the mesh 200 (74 microns).



Figure 2. X-ray diffractogram of the wastes of molding sand, the main mineral species are: Orthoclase (O), Albite (A), Quartz (Q) and Laihunite (L). Berlinite (B) and Montmorillonite (M) are the minority and residual phases, respectively.

Table 2 shows the amount found for each phase in the wastes of the molding sand. According the quantity of phases in the wastes of the molding sand, it was determined that the material has an adequate composition to be used in the manufacture of building materials, and in the ceramic industry, because these wastes of the molding sands, can be feldspar substitutes, because the high quantity of feldspar and other silicates phases like Laihunite and Montmorillonite. Furthermore, quartz content is very high and the wastes of the molding sands, also these can be used for production of silica refractories and building materials.

Entry Number	Phase	Formula	Quantity in Weight Percent
96-900-0528	Albite	(Al, Na)Si <sub>3</sub> O <sub>8</sub>	33.7
96-900-0312	Orthoclase	(Al, K)Si <sub>3</sub> O <sub>8</sub>	30.8
96-900-6304	Quartz (Anorthic)	SiO <sub>2</sub>	21.9
96-901-2075	Laihunite	$Fe_5Si_4O_{16}$	7.6
96-900-6413	Berlinite	AlPO <sub>4</sub>	4.8
96-900-2780	Montmorillonite	(Al <sub>2</sub> ,Ca <sub>0.5</sub> ) Si <sub>4</sub> O <sub>12</sub>	1.2

Table 2. Phases found in the residual sand, obtained by XRD

In Figure 3, can be seen images of residual sand particles, obtained by SEM-EDS, which notes that have a

fairly homogeneous distribution in size, showing compact particles with rounded edges without the presence of edges or sharp angles. Can be also observed in small amounts, the presence of different grain-like molten phases, which were characterized by EDS (Figure 4 and Table 3.) which proved that the material is constituted by Si, Ca and O, in form of calcium silicate; along with a substantial proportion of aluminosilicate, and iron oxide formed during the weathering of these residual sands, and before the formation of the slag.



Figure 3. Micrographs of the residual molding sands, obtained in a JEOL JSM-6300 SEM, taken at an accelerating voltage of 20 kV; a) Micrograph of the residual sand obtained at 1000 X and a distance of the detector of 16mm. b) Micrograph of residual sand obtained at 500X and a distance of the detector of 20mm.

According the composition of the wastes of molding sand, obtained by EDS (Figure 4 and Table 3), this material can be a substitute of feldspar, due to its similar composition, mainly by the silica and alumina amount that is near to that for oxides of the I and IIA groups. So it was determined that the material has a composition that can be used in the manufacture of building materials, the ceramic industry, because these wastes of molding sand, had a composition mainly based in silica, with alumina and iron oxide (6.6% wt. and 8.56% wt., respectively). Furthermore, with the sum of these two species in the chemical composition of the wastes of molding sand, have a high potential like pozzolanic material, which can be used is prepare blocks and concrete in the form of a fine aggregate. For its use in ceramics, the iron oxide removal is needed, to avoid rejection of the ceramic pieces that will be produced.



Figure 4. Spectrum obtained by SEM-EDS of the residual molding sand, using an accelerating voltage of 20 kV

Compound	Weight Percentage
SiO <sub>2</sub>	77.9
Al <sub>2</sub> O <sub>3</sub>	6.6
Fe <sub>2</sub> O <sub>3</sub>	8.56
Na <sub>2</sub> O	1.03
K <sub>2</sub> O	0.34
CaO	1.52
MgO	2.48
TiO <sub>2</sub>	0.14

Table 3. Chemical composition of the wastes of sand, obtained by SEM-EDS

#### Conclusions

The major compounds determined by XRF, are silica, alumina and iron oxide, which can help us to deduce that this is mainly clay and silica sand with slag as impurity. Furthermore, the presence of small quantities of  $ZrO_2$  could be due to that this compound was used for the internal coating of the sand mold, before being filling with molten metal.

According to sieve analysis, it was determined that residual molding sand has a grain size that is within technical specifications for direct use in the manufacture of building materials, and ceramic industry, because this wastes of molding sands can substitute fine, and also sands of medium size for concrete building materials and for ceramic industry, the wastes of molding sand can be used only with a soft grinding, to achieve a particle size near to the mesh 200 (74 microns) or lower sizes.

The controlled particle size conforms to ASTM C331 [9] and C33 [10] standards, since residual foundry sand has a fine grain size, which is within the specifications. Also, the results comply well with the Mexican standard SCT N-CMT-2-02-002/02 [11], which relates to a fine particle size.

On the basis of the analysis by SEM-EDS, it is observed that the sample of wastes of molding sand, has a fairly even distribution in size, with compact particles having rounded edges, without the presence of edges or sharp angles.

Based on this research, it was determined that the residual sand, by their chemical and mineralogical composition is potentially usable as an alternative industrial material for the manufacture of various products (brick, block, tile, refractory bricks, etc.), as well as a feldspar substitute for production of dark or reddish burnt compounds. The high amount of silica, alumina and iron oxide, that form the felsic and silicate phases inside the wastes of molding sands, have similar quantities as to be a feldspar substitute. Also the high amount of silica, alumina and iron oxide can provide a high pozzolanic potential.

A pilot testing is recommended for the production of building materials, as well as the implementation of a previous step of magnetic separation, due to the possibility of finding metal parts contained in the residual molding sand.

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