

INFLUENCE OF CHEMICAL AND MINERALOGICAL COMPOSITION OF STEELWORKS SLURRY ON PHYSICO-CHEMICAL AND STRUCTURAL PROPERTIES OF THE AGGLOMERATE

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Once with the modernization of technological lines in point of view of environmental protection, result slurry after gas cleaning found out in the form of solids in water discharged by decantation in the ponds. This residue is recovered by means of a modern station for drying and retaining at the source of the steelworks slurry. Considering that the slurry recovered contains over 45% iron, the integrated steel companies will be able to reintroduce on the technological agglomeration large quantities of dried slurry, as by-product respecting the requirements imposed when constituting batches for agglomerating tape. Along with other secondary and raw material, the steelworks slurry can have a significant contribution on quality of ferrous agglomerated used to produce cast iron.

The paper presents new research concerning the influence of chemical and mineralogical composition of steelworks slurry on physical, chemical and structural properties of the agglomerate in a view to increasing quality of the agglomerate and for reduction environmental pollution.

Keywords: slurry, properties, agglomerate, environmental pollution

1. Introduction

The wastewater from washing converter gas contains suspended solids and heavy metals such as zinc and lead. Treatment of wastewater follows to reduce the content of suspensions and prevent the fouling in the spray nozzles of transportation and treatment installations. For this purpose, the wastewater is passed through decantation installation for separating coarse particles and decanters suspensions. In the coarse separators are retained approx. 20% of the total solids. To prevent depositions in the installation the wastewater was treated with

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Na_2CO_3 . From the purification process coarse slurry is obtained which is recovered directly from the coarse separators in the sludge drying and retention station [1].

The steelworks slurry and dust were analyzed from point of view of physical and chemical properties for the determination of the constituent elements and their compounds. These determinations are important for its introduction in the agglomeration process of iron and manganese ores to obtain the agglomerate necessary for making of cast irons in the blast furnaces [2]. The main components of the slurry are Fe, CaO and SiO_2 , which would considerably reduce the consumption of raw materials, respectively iron ore. Modern equipments recover solid suspensions as slurry from water discharged and from the purification gas with a view then to use it as a by-product in the agglomeration process. The steelworks slurry contains over 45% iron and its use can reduce consumption of raw materials, respectively the iron ore [3].

The production of agglomerate with a lower SiO_2 content is one of the basic conditions in the cast iron production with low-percentage silicon [4]. The concentration of constituent elements and different compounds of the steelworks slurry may alter the morphological structure and physico-chemical properties of the agglomerate [5]. The interest in the research on the steelworks slurry is due to their ability to form complex ferrite at existing temperatures in the agglomeration process, thus improving the quality of the ferrous agglomerate [6].

By using steelworks slurry in a well-established amount in the recipe that forms the basis of the agglomeration batching, it is possible to reduce the negative impact of these reusable materials on the environment protection [7]. To achieve research concerning the influence of chemical and mineralogical composition of steelworks slurry on agglomerate's physical-chemical and structural properties were analyzed samples of steelworks slurry and agglomerate.

2. Materials and methods

The chemical and mineralogical composition of the steelworks slurry and agglomerate as well as the structural analysis was determined by XRF analyzes. Morphological and structural characterization was performed by microstructural analysis, Scanning Electron Microscope (SEM), and by energy dispersive X-ray microanalysis (EDAX and X-ray diffractometry. For XRF analyzes the steelworks slurry samples were prepared by two methods: pressing method and the melting method in order to be determined at spectrometer ARL 9800 XP, X-ray fluorescence spectroscopy. In case of the preparation of the samples by pressing it's used to be a flux (lithium tetra borate in a concentration of 10 times higher than the sample).

The mixture is homogenized and inserted in a plastic capsule. The capsule is inserted, in its turn, in a metal container with cover. The plastic capsule is introduced at a press and subjected to a force of 10-30 t/f. The samples are kept in press approx. 5 minutes after which are preparing for chemical analysis. For sample preparation by fusion it's used to be the same binder, in the same proportions as the samples by pressing, then are inserted in an oven combustion IR, type LECO CS-200, or type VULCAN – Fusion Technology produced by HD Electronic, provider for applied in XRF solutions.

3. Results and discussions

The work shows the influence of the chemical and mineralogical composition of steelworks slurry upon the quality of the ferrous agglomerates and analyses through special techniques slurry and agglomerate samples in a view to obtaining favourable results by using this by-product in the sintering process.

Chemical composition of slurry analysed by XRF method

The experimental results concerning chemical composition of slurry are presented in Table 1 for two cases.

Table 1
The chemical composition of the steelworks slurry

Sort	Used method	Chemical composition (%)								
		Fe	Mn	SiO ₂	CaO	MgO	Al ₂ O ₃	ZnO	FeO	Fe ₂ O ₃
slurry	Pressing	48.50	0.69	3.04	24.20	0.29	0.28	0.04	49.46	53.62
	Melting	49.90	0.72	3.18	24.80	0.30	0.29	0.04	50.89	55.17

The differences between these two methods, by pressing and melting are insignificant, is therefore recommended method of preparing samples by melting as it's used to be the temperature 1270°C that provided on the sintering machine. The sort's properties from the agglomeration batch (heat, conductivity, porosity, density, particle size of load component) have influence on heat exchanging process in the layer of burning. The slurry granulation as well as its humidity or other materials subjected to the agglomeration process, determine the height of the layer on the agglomeration band and the stability of this under the action of depression of the sintering installation.

XRD analysis of the steelworks slurry

The qualitative analysis of the phases was achieved by means of X-ray diffractometer Panalytical X'Pert PRO MPD. In the histogram of Fig. 1 is presented semi quantitative analysis of the slurry samples compounds.

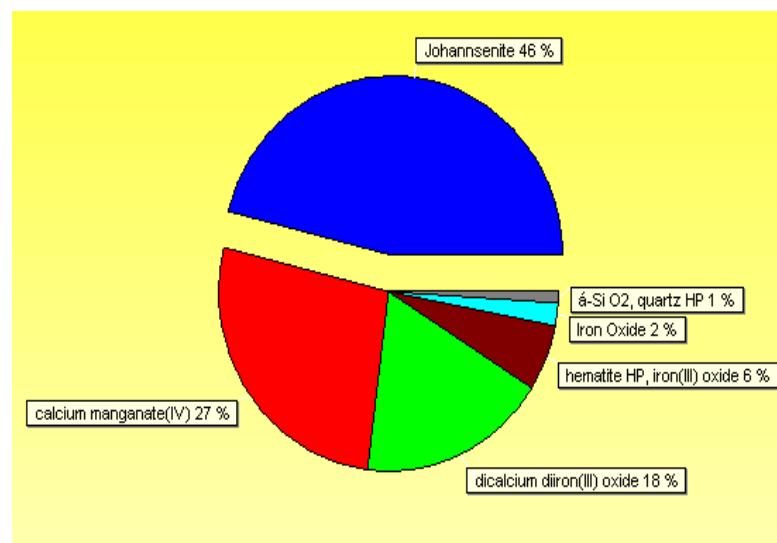


Fig. 1. Histogram concerning of semi quantitative analysis

XRD analysis of the agglomerate

The reducibility is characteristic of the secondary and raw materials during the processes carried out in the furnace. It depends on the oxides nature and a series of thereof physical properties. The presence of magnetite of a high concentration makes the resulting agglomerate hardly reducible, but the presence of hematite (Fe_2O_3) favouring the growth of reducibility. In Fig. 2 is presented the diffractogram on the agglomerate samples.

Indexing diffractogram reveals next 6 phases:

- $CaFe(Si_2O_6)$ (calcium iron silicate) with monoclinic crystalline system having the maximum of the peak at the angle $2\theta = 29,989^0$;
- $MgFe_2O_4$ (magnesia-ferrite) with cubical crystalline system having the maximum of the peak at the angle $2\theta = 35,442^0$;
- Fe_2O_3 (hematite)
- Fe_3O_4 (magnetite)
- $CaO \cdot SiO_2$ (calcium silicates)
- $CaO \cdot 2Fe_2O_3$ (calcium ferrites)

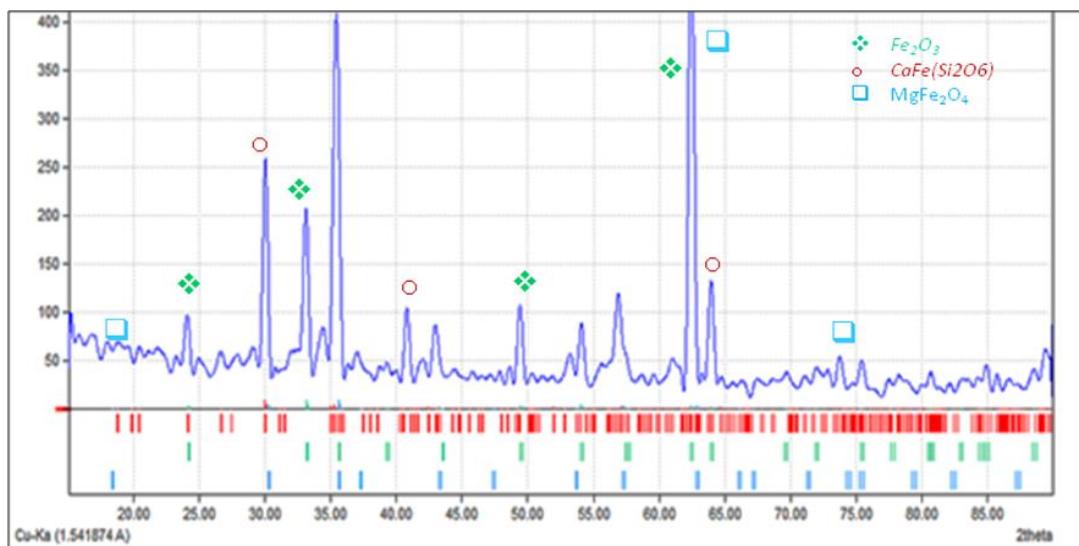


Fig. 2. X-ray diffractogram (indexed) obtained on the agglomerated sample

In the presence of silicon dioxide (SiO_2) and ferrous oxide (FeO) fayalite (Fe_2SiO_4) formed which is easily fusible because has a melting temperature of 1209°C . The fayalite and other easily fusible compounds passed as a liquid phase that melts other compounds from the charge, so that makes sintering agglomerate to have high mechanical strength. The agglomeration batch containing lime stone and lime conducted to autofondant agglomerate. In these conditions are favoured the reactions from which results $\text{CaFe}(\text{Si}_2\text{O}_6)$ and FeO. The autofondant agglomerate has a higher reducibility than customarily agglomerate.

Chemical and microstructural analysis by scanning electron microscopy

Analysis of the slurry samples were performed by electronic microscopy on the samples surface, known as Scanning Electron Microscope (SEM). In Figs. 3, 4 are presented the SEM micrographs of slurry samples.

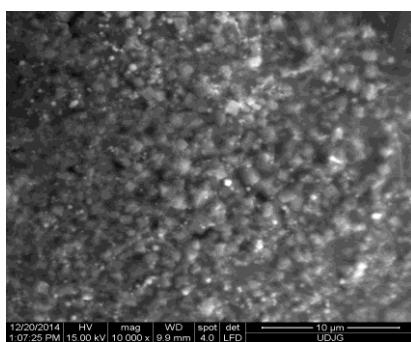


Fig. 3. Slurry sample achieved by pressing

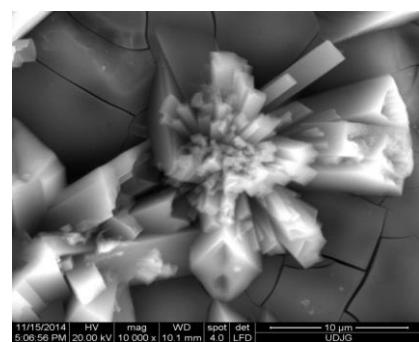


Fig. 4. Slurry sample achieved by melting

Powdered slurry samples from Fig. 3 indicate that the particles have different dimensions and shapes, some of them rounded other polyhedral. The slurry samples Fig. 4 highlights formation of the new phases at the limits of the particles with the columnar and fibrous shapes. It was used the technique by melting samples for accuracy of the obtained results. In Fig. 5 is presented X-ray spectrum that reproduces elemental analysis by SEM – EDAX.

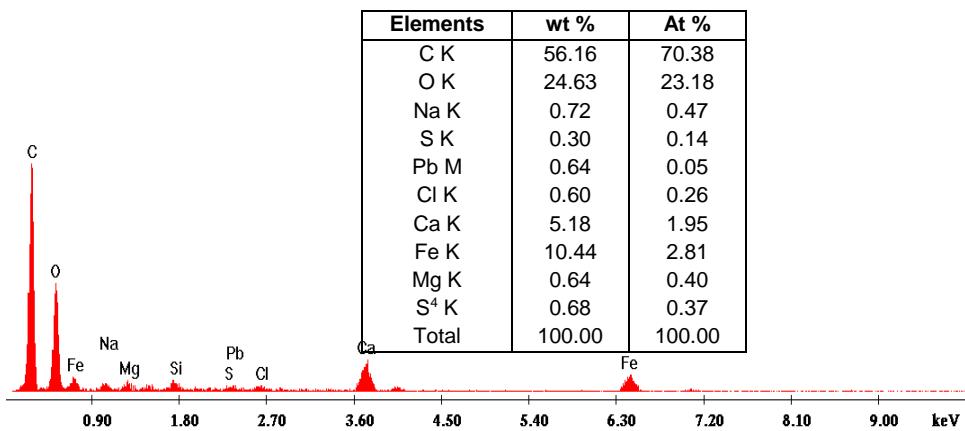


Fig. 5. X-ray spectrum for steelworks slurry sample obtained by melting

Figs. 6, 7 present the microstructures of agglomerate samples performed by Scanning electronic Microscopy (SEM)

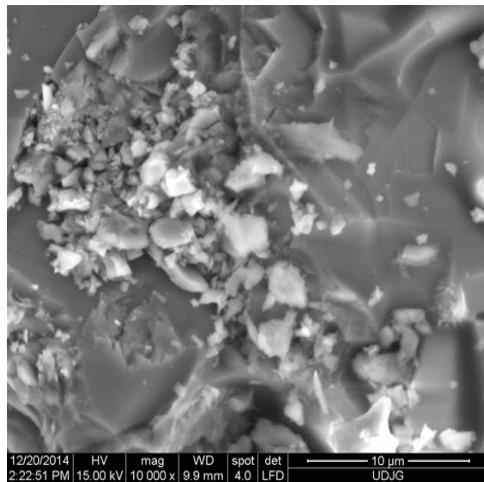


Fig. 6. SEM image on agglomerate sample

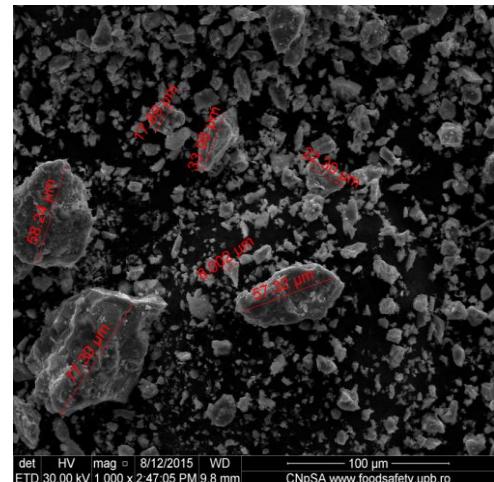


Fig. 7. SEM image on agglomerate sample

The structure of the agglomerates chilled at normal temperature are highlighted hematite (Fe_2O_3), magnetite (Fe_3O_4), silicates of calcium ($\text{CaO}\cdot\text{SiO}_2$)

ferrites of calcium ($\text{CaO}\cdot 2\text{Fe}_2\text{O}_3$) and calcio-ferrous olivine ($\text{CaO}_x\cdot(\text{FeO})_{2x}\cdot\text{SiO}_2$). Can be observed the differences that appear in the formation of the grains and distributing them (isolates or compacts).

Following the analysis that was performed on the surface of the agglomerated sample whose micrograph is shown in Fig. 7, and using the EDAX technique the distribution map of the chemical elements was highlighted, Fig. 8.

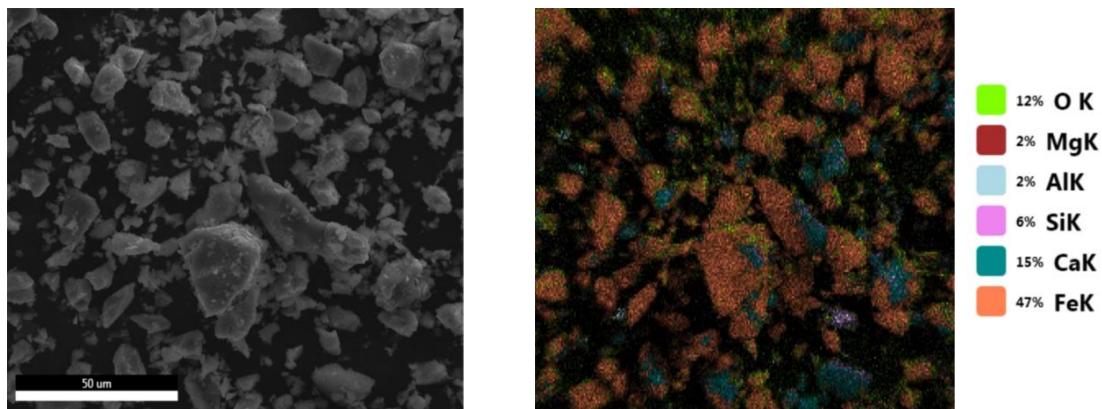


Fig. 8. Distribution map of chemical elements on the surface of the agglomerate sample

The presence of silica and calcium oxide in the analyzed raw materials and in the other stack assortments directly influences the physical and chemical properties of the agglomerate and its basicity. The ratio CaO/SiO_2 is a basic criterion in calculating the metal load for cast iron production. These determinations are important for the introduction of the steelwork slurry into the agglomeration process (in appreciable amounts) for making of the agglomerate required to obtain the cast iron in the furnace.

4. Conclusions

As a result of the experiments the following conclusions resulted:

- The ability to synthesizing of slurry is higher than that of ores with large granulation because the dust particles melt more easily in their contact points so that forming liquid phases;
- The chemical composition and granulation of steelworks slurry it's very important in the sintering process because influence the formation of binder phases agglomerate;
- The iron content of recycled material studded exceeds 45% fulfilling the condition imposed for its introduction in the process of agglomeration;

- The constituent elements of steelworks slurry can modify morphological structure of the agglomerate;

- Interest for testing on the steelwork slurry is due their property to form the ferrites complexes at the temperatures in the sintering machine, ferrites that improve physical and chemical properties and reducibility of the ferrous agglomerate.

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