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SIDERURGY SLAGS RECOVERY IN BUILDING INDUSTRY

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ABSTRACT

During the metallurgical processes of iron and steel elaboration, besides the basic products, it results a serious of secondary products (wastes) in high quantities but with a high recycle – recovery potential, and their reintroduction in the economic circuits. In this paper, we are going to refer strictly to the working and the recovery of the blast furnace slags, respectively to LD converter slags, without insisting on the formation mechanism and slag reactions.

KEYWORDS: slag, recovery, magnetic separation, ferrous particles

1. Introduction

The blast furnace slags got variety of uses, both in state directly worked in the metallurgical plants in a non-processing cool state. Having in view the technological demands of the fabrication process of the cements, especially from point a view of the finesse crushing as well as of the chemical composition, in this respect it is imposed in advanced iron elimination of the converter slag.

2. The blast furnace slag

The totality of the non-reductible oxides as well as different metals combinations enter in the structure of the blast furnace slags.

The sterile of the iron ores as well as the coke ash contain mainly SiO_2 and Al_2O_3. In order to raise the stability of SiO_2 and also the other non-reductible compounds in the slags, in the furnace process, CaO is introduced either through limestone directly in the furnace charge by means of the agglomerate. For the same goal and also for the improvement of the slag properties the MnO is used.

The introduction of the CaO and MnO in the furnace charging is made in a well balanced ratio, correlated with the SiO_2 and Al_2O_3 contents, brought by the metallic charge and cokes.

The reason for the flux introduction is based on the formation of complex chemical combinations with low melting points, smaller than of every oxide in the composition taken separately. In the furnace slags these, as main components, cover about 90% from the totality of constituents.

The ratio between the calcium and magnesium oxides and that of acids oxides, meaning SiO_2 and Al_2O_3, represents the degree of chemical activity of the slags known under the name of basicity number.

Basicity number can be analyzed under many aspects, function of the number of base oxides, respectively acid oxides which were taken into consideration. In order words, the whole basicity number can be calculated by using the following relation:

$$I_b = \frac{(CaO + MgO + FeO + MnO)\%}{(SiO_2 + Al_2O_3)\%} \qquad (1)$$

For the current usage conditions utilization, the appreciation of the slag basicity is made only by simple ratio:

$$I_b = \frac{(CaO)\%}{(SiO_2)\%} \qquad (2)$$

The acid slags are recognized by the filiform aspect during the following process; they have a glassy aspect, brown when they are enough hot or dark brown towards black when they are cold, the content of the FeO for these ones surpassing 2-3% in composition. The basic slag generally recognized with values of 1.2-1.4 of the basicity number given by the ratio CaO/SiO_2 are much higher, the crystalline lattice is breakable during the following processes, they are more fluid, gather an important quantity of heat because of special refractoriness. In Table 1 several chemical compositions of some furnace slags are given.

Table 1. *The chemical compositions of some furnace slags*

Sample	Composition, [%]						
	SiO_2	Al_2O_3	CaO	MgO	MnO	FeO	CaS
1	28.1	22.1	41.14	3.0	0.46	0.20	5
2	32.11	15.06	45.17	1.0	0.45	0.21	6
3	32.42	12.16	46.37	1.2	0.7	0.75	5
4	38.40	10.10	41.9	2.5	1.88	0.22	5

The blast furnace slags processing

The most used working procedure of the blast furnace slags is granulation, the product having uses especially in a cement industry. The crystalline slag can be used for the pavement fabrication or in roads building, after having been breakable.

The slags which have a high content of CaO can be used in agriculture, for acid soil treatment. The expansion slag can be used as a thermo-isolator in building industry. The slag as a glass wadding can be used also as a thermo-isolator.

3. The LD converter slag

At the steel elaboration in LD converters, taking as example Arcelor Mittal Steel Galati, important slag quantities result. The characteristics of this slag are much more different from those of blast furnace slags. These differences consist both in the chemical composition and in working possibilities.

Because these slags contain also iron in free state there is no possibility of a sudden cooling through granulation and expansion. In the chemical composition, the LD converter slag we have FeO 16-22%; SiO_2 8-12%; CaO 41-53%; MgO 1-3%; Al_2O_3 3-5% and others.

The processing of LD converter slag

Because of its composition, the LD converter slag has another working technological process as follows: the liquid slag is transported by means of slag ladle towards the slag dump where processing takes place; in this place the slag ladle are poured out, in the working front where, for two weeks, the slag is sprayed with water in order to be cooled. After the cooling process it is taken with excavator and it is poured out in the maturation front. In these fronts, the slag will stay six months while, periodically, it is sprayed with water. In this way a part of calcium oxides and other levigables components are eliminated.

At the end of the maturation process, the slag enters in the working cycle which contains more technological operations such as:

- excavation and transport at the processing plant;
- sorting and eliminating rough iron;
- breakage;
- magnetic separation of ferrous components;
- sorting on particle size range;
- dispatch to customers.

The aggregates resulting from this process, called „LIDONIT" have a high hardness and it is useful for roads building, roads repairs, ditches and billows protection, hydro-technical works.

4. The obtaining of the cements from metallurgical slags

Taking into account the physical and chemical properties of the metallurgical slags, mentioned above, we began from the idea of eliminating the iron (under free form and under oxides form) and the calcium oxides from the steel works slags; the remaining quantity can be used as raw materials basis for some refractory products.

Two kinds of Lidonit were used for making experiments. After a fine divided crushing of the two samples, there were made chemical analyses in the laboratory. In Table 2 we can see the composition of the two samples.

Table 2. *The composition of the samples*

Sample	Fe	Mn	SiO_2	CaO	MgO	Al_2O_3	PC
	[%]						
Sample 1	22.64	5.49	11.49	41.20	1.95	3.70	abs.
Sample 2	22.50	5.56	11.35	41.28	1.76	3.80	abs.

After the chemical analysis it followed the sampling of 100g from each sample, $\pm$ 0.001g.

Both samples were magnetically separated, in order to eliminate the iron, obtaining the following results: -sample 1: from 100g were magnetically separated 31.4g and remaining 68.6g.

- sample 2: from 100g were magnetically separated 31.4g and remaining 69.9g.

After this separation, it followed a new set a chemical analysis for the processed samples, the results are shown in Table 3.

Table 3. *The composition of the samples*

Sample	Elements, [%]						
	Fe	**Mn**	**SiO_2**	**CaO**	**MgO**	**Al_2O3**	**PC**
Sample 1 A (31.4 g)	76.35	2.54	5.75	4.56	1.04	1.85	abs.
Sample 2 A (68.6 g)	5.91	3.52	15.56	48.47	2.24	6.53	abs
Sample 1 B (30.1 g)	72.87	2.28	6.12	4.98	2.07	2.15	abs
Sample 2 B (69.9 g)	7.27	4.01	17.24	49.11	2.69	7.01	abs

Then, we had in view eliminating the calcium oxides from sample 2A, respectively, 2B, by combining them with water; according to the reaction $CaO + H_2O = Ca(OH)_2$, at one of the samples, there is a small quantity of water, after about 48 hours, this one was subdued to a series of hydrolyze reactions, after which a dense and tough mass was made similar to cement.

In order to find new opportunities for high recovery of the metallurgical slags, with the aim of obtaining some common cement, at acceptable price – quality ratio, we are going to refer to some information from the cement industry and construction materials.

Hidratation of the mineralogical component of a cement

The cement is obtained by calcinations a mixture of chalkstone and clay in adequate proportions in order to obtain the final requested composition.

The components, finely crushed and well mixed are burnt in tubular rotary furnaces, at 1400 – 1450^{0}C. The material which, after a beginning of melting process, takes the shape of brown (clincher) grains, is then crushed very fine (15% residues on the separating screen with 4900 hole on cm^2), an important operation for obtaining a good quality.

The cement is a mixture of calcium basic silicate, calcium aluminates and ferrous calcium.

The strengthening of the cement during the hydration process takes place because of the formation of hydroxides and aluminates calcium, while the silicates are transformed into calcium colloidal hydro-silicates, by means of which the mass adherence is made.

The hydration – hydrolyze of the calcium silicates

The cement being a silicate binding, the hydration - hydrolyze of the calcium silicates has an essential role in the strengthening process. From the two calcium silicates components of the Portland cement the tri-calcium silicate and bi-calcium silicate, the first presents, in comparison with water a much higher reactivity (capacity of hydrolyze) at the interaction with water of the calcium silicates, at the beginning on the binding grains surfaces are formed a calcium hydro-silicate rich in the calcium oxide with the ratio Co / SiO_2 (C / S) similar to that of the anhydride substrate (hydrate I) which is later transform the with high speed in a slow basic hydro-silicate – hydrate II (C/S $\approx$ 0.8 – 1.5), this one transforming in a stable hydro-compound - hydrate III (C/S $\approx$ 1.5 – 2). The products of the interaction between the calcium silicates and the water present forms with different degrees of ordinations, with very small submicroscopic dimensions (gels).

The ratio CaO/SiO_2 of the hydro-silicates from straightened calcium silicate paste depends, especially, on the hydration. Under normal conditions of temperature and pressure, it is stated, generally, that the final value of the ratio C/S is between 1.6 and 1.9. Although the composition of the phases existing in paste of 3 $CaO \cdot SiO_2$ (C_3S) and β-$2CaO \cdot SiO_2$ (C_2S) is the same, the ratio which are establish between them are different, is emphasized especially the bigger proportion of calcium hydroxide from the paste of tri-calcium silicate (C_3S).

The tri-calcium silicate interact quickly with water, thus in a couple of minutes around binding grains is appears a network of fibrous calcium hydro silicates.

These forms grow and fill rapidly spaces between the grains of tri-calcium silicate. The specific surfaces of the calcium hydro silicates from the calcium silicate pastes which straighten, the surfaces correlated with its structural compositional characteristics is between 1x10^5 and 4.5x10^5 m^2/kg, fact that leads to a medium size of the particles (considered spherical) of 80 – 100Å. The specific surfaces decrease at the same time with growth of molar ratio CaO/SiO_2. Aluminates and calcium ferrite-aluminates influence in a high degree both the straightening process and the properties of the cement stone. The tri-calcium aluminates are characterized by interaction speeds with water higher then calcium silicates. The chemical composition of the cement is given in Table 4.

Table 4. *The chemical composition of the cement*

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3	CO_2+H_2O
18-26%	4-12%	2-5%	58-66%	1-5%	0-2%	0.5-2.5%	0.5-5%

4. Experimental results

Following these aspects we can notes some similarities regarding the composition of the metallurgical slags and of the Portland cements. By using both kinds of slags (furnace and LD converter), in some proportions through very fine crushing in ball mills and by adding some additive (sodium silicate, gyps, lime) it is possible to obtain a kind a cement with good properties but with a low cost. In this way we raise the value of the slags and of the slags aggregate which now are sold with 4 – 6 USD / tons.

In the practical experiments from the same samples lot we pasted to a crushing and a magnetic separation of the iron.

Up to now these were made experiments on four different dosing and on there basis they were made the same number of samples.

The samples were made in conformity with SR EN 196-1 and SR EN 196-3 / 2002, with the dimensions shown in Figure 1.

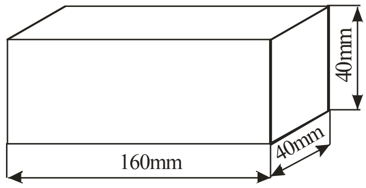

Fig.1. *Sample dimensions*

For the experiment they were made the following samples:

1. Lidonit (570g) + $CaSO_4 \cdot H_2O$ (30g) + water (285g);
2. Lidonit (510g) + $CaSO_4 \cdot H_2O$ (30g) + CaO (60g);
3. Lidonit (250g) + granulated slag (250g) + CaO (50g) + gyps (50g);
4. Lidonit (230g) + granulated slag (230g) + cement (50g) + CaO (60g) + gyps(30g).

In Figure 2 it is represented a plant of magnetic separation; which can achieve a iron separation about 99%.

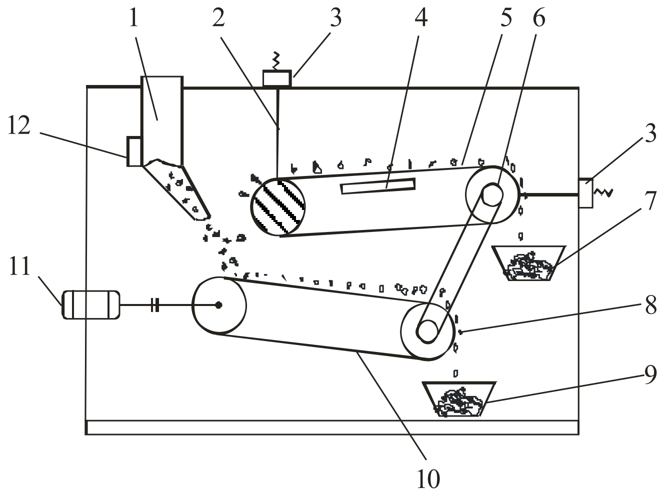

Fig. 2. *Plant for magnetic separation: 1-powders bunker; 2-rotor; 3-system for tension of the strip; 4-demagnetizor; 5-superior strip; 6-wheel for strap; 7-vat for ferrous particles; 8-mineral particles; 9-vat for minerals; 10-inferior strip; 11-motor; 12-vibrating machine*

5. Conclusions

Having in view the technological demands of the fabrication process of the cements, especially from point a view of the finesse crushing as well as of the chemical composition, in this respect it is imposed in advanced iron elimination of the converter slag. Regarding the separation of the iron from the slag we can use successfully a magnetic separation plant of the steel powders resulting from the finishing operation.

This metallic powder contains a quantity of mineral components torn off from rectification stone during the chip less process (Al_2O_3 and SiO_2). Removing the mineral components included in the metallic powder is made with special plant based on magnetic attraction phenomena.

Another economic advantage regarding the above mentioned things is represented by the recovery of the ferrous particles magnetically separated. Having in view the fact that the separated metallic fraction contains over 70% Fe and iron oxides, these can be sending to the Agglomeration section or it can be combined with the cokes powder from UCC and, in the presence of a binding, to be made ferro-coke briquette.

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