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RECYCLING POSSIBILITIES OF METALLURGICAL SLAG

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ABSTRACT

The target of the current metallurgical industry is to recycle and utilize all their by-products. Slags are the important wastes and by-products of metallurgical industry, which have been treated, recycled and used worldwide. The present paper summarizes results obtained from physical and chemical analyses on blast furnace slag. The physical structure and gradation of granulated slag depend on the chemical composition of the slag, its temperature at the time of water quenching, and the method of production. The chemical reaction between blast furnace slag and water is slow, but it is greatly enhanced by the presence of free calcium oxide and free magnesium oxide getting on calcium and magnesium hydroxide. These alkalis can modify the mechanical properties of slag. It is very important to analyze the content of the free calcium oxide and free magnesium oxide. Blast furnace slag is mildly alkaline and exhibits a pH in solution in the range of 10 to 12. Processed slag exhibits favorable mechanical properties for aggregate use including good abrasion resistance, and high bearing strength. By our assessments it was proved that the blast furnace slag from S.C. “Arcelor Mittal Galati” S.A. have comparable properties of granite. This fact will allow utilizing the slag aggregates on the road construction, railway embankments, hydrotechnic constructions.

KEYWORDS: blast furnace slag, mechanical properties, abrasion resistance

1. Introduction

The global warming effect and natural resource saving are the general environmental topics nowadays. In addition, the land filled with the waste materials has become a significant source of pollution of air, water and soil, and further adversely affects the human health, and the growth of plant and vegetation. From the viewpoint of preservation and protection of the global environment, slag recycling has attracted the attention of many scientists in recent years. Boom reviewed the recent research trend on slags and found that there is significant increase in studies on recycling of slags and their environmental problems.

Slag plays an important role in the metallurgical process as it has to ensure the complete separation of the metal from ore. Moreover, it has a refining role – to render soluble the elements which, in general, have to be removed from metal. A refined slag has to render soluble, the more the better, the sulphide so that the sulphur concentration in cast iron and steel should be as small as possible. An important factor in differentiating slag is the treatment applied during cooling which leads to differences in the use of slag. Metallurgical plant slag is the main source of waste which can be recycled on location. By limiting the capacity of the wasteyards, the disastrous impact on the natural equilibrium and environment is reduced. The study of slag has as a result the valorization and, implicitly, the diminution of the necessary quantity of natural ore extracted from lithosphere, the lessening of environmental degradation by establishing extraction pits. Due to the large slag quantities and the stricter environmental regulations, recycling and utilization of these slags are an attractive alternative in order to reduce and eventually to eliminate the disposal cost, to minimize the related environmental pollution, and to save the resource conservation.

2. Materials and methods

Physico-mechanical analyses

The main physical-mechanical analiyses made at SC DSU ROMANIA SRL Galati on the metallurgical slag were:

- Density(g/cm³) SR EN 1097-3/2002 and SR EN 1097-6/2002
- Volume stability SR EN 1744-1/2004

- Compressive strength (%mass losses)and ($N/mm^{2)}$ SR EN 1926/2000
- Impact strength (%mass losses) SR EN 1097-2/2002
- Water absorption(%) SR EN 1097-6/2002 and SR EN 1625/2000
- Polished stone value PSV SR EN 1338/1339/1340-2004
- Wear resistance- Los Angeles (%mass losses) SR EN 1097-1/1998
- Freeze –thaw resistance (%mass losses) SR EN 1367-1/2002; 10 frost-thaw cycles in the temperature range (-20ºC /+20ºC).
- Granulometry of the mixture of granulometric sorts, SR EN 662/2002 and SR EN 667/2004
- Electrical conductivity(mS) SR EN 1744-1/2004

Chemical analyses

Chemical reagents of type p.a. were used in the chemical analyses. The main reagents acquired and used are: H_2SO_4, HNO_3, HCl, Na_2SO_4, $MgSO_4$, $CaCl_2$, BaSO4, ethylene glycol, acquired from SC Chimopar SA Bucharest, indicators (methylorange, phenolphthalein, tymol blue) from SC Sinteza SA Oradea. Methods adapted to the European standards were used for the analysis of the oxide percentage of slag.

- The determination of free CaO and MgO was carried out in accordance with SR EN 1744-1/2004 through acidimetry, conductometric analysis, as well as through constancy of volume measurement and in the case of the conplexonometric method STAS 4605-9/1988 and STAS 4605-10/1980 were used.
- FeO and Fe_2O_3 were determined in accordance with SR ISO 2597-1/2001 and STAS 1574-3/1990.
- SiO_2 determination was made in accordance with SR ISO 2598-1 /1996; S was determined in accordance with SR ISO 4690/2001
- MnO was determined in accordance with SR ISO 1574/1994
- Al_2O_3 was determined in accordance with SR ISO 4687/2001
- CaO and MgO total quantity determination was carried out in accordance with SR 6482/2002 and SR EN 196/2002

The determination of pH was carried out with the OP-264 pH-meter, existent in the laboratory, whose calibration was made with a solution of known pH (pH- 4, 7, and 8) (citric acid solution + Na_2HPO_4)

The resistance to the gelivity test (frost-defrost) was determined from a chemical point of view by treating metallurgical slag with saturated solutions of Na_2SO_4 or $MgSO_4$ (under the form of ten cycles of immersion-drying). In both processes applied to metallurgical slag, the values obtained with regard to resistance are the same although the substances used have different molecular weight.

3. Results and Discussions

The following mineralogical components resulted from the chemical analysis of metallurgical slag: cristobalite (SiO2)(*1*); gelenite (2Cao*Al2O_3*SiO_2)(*2*); corundum (Al2O3)(*3*); sillimanite (Al_2O_3*SiO_2)(*4*); pyrope (3Mgo*Al_2O_3*3SiO_2)(*5*); dicalcium ferrite(*6)*; calcium orthosilicate (*7*) (*table 1*) Theoretically, steel slag should be chemically inert because of its crystallized minerals content (dicalcium silicate- β and γ polymorph forms, dicalcium ferrite, wüstit, magnetit), minerals that do not react with any fluids usually in contact with in the normal environmental condition(rain water). The main oxides existent in ferrous metallurgical plants are rendered in percents as obtained through the analytical quantitative determinations (*table2).*

***Table 1**. The mineralogical composition of metallurgical slag compared to natural rocks*

The mineralogical composition	u.m.	Metallurgical slag	Natural rocks
Cristobalite(1)	%	30-36	32-38
Gelenite(2)	%	8-10	10-12
Corundum(3)	%	2,5-5	3-6
Sillimanite(4)	%	4,5-6,5	4-5,5
Pyrope(5)	%	2-4	3-5,5
Dicalcium ferrite(6)	%	1-2,5	0,5-1,5
Calcium orthosilicate(7)	%	1-2	-
Wüstit(8)	%	0,5-1	<0,5

***Table 2**. The oxidic composition of metallurgical slag*

Metallurgical slag	CaO	MgO	SiO_2	Al_2O_3	S	Fe_2O_3	FeO	MnO	Other oxides
	%								
Blast furnace slag	41	7-8	36	7-9	0,8	0,5-1.5	0,5-0,8	0,2-1	~1,3 (P)
Steel slags	42-44	5-7	30-35	2,5-3,7	-	15-20	2,5-5	3-6	-0,5 (Cr and V)

Apart from the above mentioned oxides in the composition of steel mill slag there are also to be found free oxides such as Ca and Mg oxides, whose percentage presence in the slag composition has to be as small as possible since, in contact with water, the following chemical reactions take place:

CaO free + $H_2O \rightarrow Ca(OH)_2$

MgO free + H2O$\rightarrow Mg(OH)_2$

which would make the aggregates obtained through slag processing disintegrate (under the above mentioned condition).

The elimination of this problem is effected through controlled cooling of the slag and through its ageing, meaning, the continuous watering of it for approximately 6 months so as to ensure consistency of volume of the aggregates obtained during the mechanical processing of crude slag. Figure 1 represents the comparative graph regarding the constancy of volume of two slag samples which indicates the role that ageing has (that is, eliminating Ca and Mg free oxides.

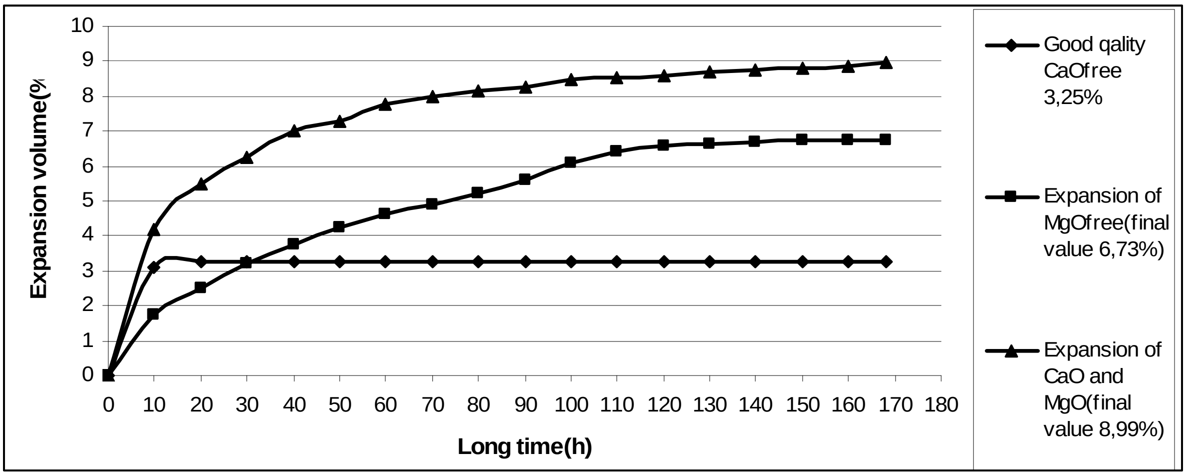

***Figure 1**: The constancy of volume of metallurgical slag*

The presence of Fe (+2) and Fe (+3) →Fe (total) oxides in the metallurgical slag composition makes its gross density be greater thus being possible to compare it to natural rocks.

Table 3 gives the density values obtained through determinations.

***Table 3**. Metallurgical slag density compared to natural rocks*

Physico-mechanical characteristic	**Aggregate type**		
	Metallurgical slag	Granite	Gravel
Gross density(g/cm³)	2,600-3,500	2,800	2,600
Refined state density (g/cm3)	1,650	1,400	1,300

During the determination of the resistance to frost-defrost (chemically and physico-mechanical) very similar values were obtained through both processes due to the slow cooling process of metallurgical slag and implicitly to the formation of its crystalline structure.

The slow cooling process is also essential for obtaining the porosity close to that of natural rocks.

Slow air cooling favours to a great extent crystallization but, at the same time, allows the unfolding of polymorphic transformation reactions of type β calcium silicate into γ calcium silicate in basic slag *(the pH of ferrous metallurgical plant slag varies from 10 to 12).*

Through the same system of slow cooling from the metallurgical slag state of fusion, under atmospheric conditions or through successive watering, these materials are ensured with a high level of homogenous cristallinity, high physico-mechanical resistance, and in general, properties that can be compared to those of aggregates obtained from natural rocks.

Metallurgical slags contain mainly silicates and they are provided by metallic melt solidification. Any slag has the main role to render soluble as much sulphur gases as it’s possible and all other minerals that are not desired into metallic melt (iron and steel). There are two kinds of metallurgical slag: furnace slag resulted on iron works and steel slags. At it turn, there are three kinds of steel slags all depend on the type of furnace atmosphere it is used: Linz-Donawitz converter, where it is produced LD steel slag, electric-arch furnace, where it is produced EAF slag, and ferro-chromium slag produced also into electric- arch furnace. After separation from the melted steel, the liquid slag is discharged into a pit, where the slag start to cool, slowly under natural condition of humidity, for minerals crystallizing and chemical stabilization.

After a period of six month of maturation, the raw slag is crushed and sieved into a special factory equipment, and carried out in a special storage place. Prepared in this way, LD steel slag aggregates have the proper characteristics to be used in road construction field, railway construction, waterway construction and civil engineering as well (table 4).

Table 4. *LD steel slag aggregates characteristics comparing with natural aggregates*

Characteristics		**Type of aggregate**			
PROPERTY	**U.M.**	**BOS steel slag**	**Basalt**	**Granite (monolithe)**	**Requested under German norms for road construction**
Apparent density	[g/cm^3]	>3,2	~2,95	~2,70	-
Volume increase-steam test	[%]	<1 - <3	-	-	<5 $^{4)}$
Water absorbtion	[%]	0,3-0,9	<0,5	0,3-1,2	<0,5
Impact strength sorts 8/11 mm	[%(m)]	15-20	9-20	12-27	<18 $^{1)}$ <22 $^{2)}$ <34 $^{3)}$
Compression strength	N/mm^2	>130	>230	>160	-
Bulk density	[g/cm^3]	1,5-1,6			-
PSV	PSV	54-57	45-56	45-58	>43
Thaw- freeze resistance	[%]	< 0,3	< 0,8	0,8-2	< 3,0
Environmental compatibility- pH		10-12	-	-	10-13
Electrical conductivity	mS/m	<300	-	-	<500
Cr ^{IV}	mg/l	<0,01	-	-	<0,02
Wear resistance- Los Angeles	[%]	<18	<20	<12	10-20

The results of the analyses carried out indicate that the slag under study has a composition and properties similar to natural rocks. Hence slag can be mechanically processed (crushed and granulometrically separated) into aggregates similar to those obtained from natural rocks. Broken stone is obtained in this way with dimensions ranging from 4 to 8 mm; 8-16 mm;16-25 mm; big broken stone with granular dimensions ranging from 25 to 63(80) mm; as well as mixtures of granulometric varieties(*broken stone ballast*) the granulosity ranging from 0 to 31,5 mm or 0-63 mm. The granulometry thus resulted (eg. 0-63 mm) falls within the granulometric curbs prescribed by SR EN 662/2002 for the ore used in road construction. Apart from broken stone and mixtures of granulometric varieties, crush sand is also obtained at a granulosity of 0 to 4 mm, being possible to use it instead of natural sand (river sand).

Due to a slow and steady cooling some slag achieve a high level of homogenous cristallinity which give them a very great resistance to compression and breaking (with a loss of only 5 to 6% in weight during the processing), fact which makes it impossible for this slag to be processed (through crushing) resulting in grains of big dimensions such as 45-125 mm;63-180 mm;90-180 mm;45-180 mm; 90-250 mm, dimensions which correspond to natural rocks (coarse aggregates) used in hydro technical constructions or bank protection in accordance with SR EN 13043/2003.

4. Conclusions

Being obtained from crude slag through crushing, aggregates have sharp edges and angles that is, a high roughness and, as a result the adherence to any binders (bitumen or hydraulic binders) is excellent which means that they are ideal in road construction [7].

The presence of SiO_2 in slag composition gives it the properties of a hydraulic binder (that is why blast furnace slag is currently used in the making of cement).

Due to the high resistance to gelivity (frost-defrost), as well as to the high gross density, the aggregates obtained in this way are ideal in hydro technical construction works, these being hard to "wash" by the water currents. [9]

The characteristics regarding the form of the grains (measured with the sliding calipers) and the coarse surfaces of aggregates make it possible to obtain the necessary bearing capacity and even to exceed the values specified in standards for the making of layers resistant to frost or bearing layers of *macadam* type (crushed stone surface, calibrated, of monogranular variety, laid and cylindrated up to clamping first under dry conditions, fastened through colmation by water and aggregation material (crushed sand) and then cylindrated until definitive fastening [3,4].

All the results obtained through chemical and physico-mechanical determinations correspond to the technical quality requirements for aggregates used in road construction and specified in SR EN 13242/2004

Moreover, aggregates from metallurgical slag can be successfully used in the making of railway beds, giving the respective constructions durability and resistance in accordance with SR EN 13450/2000.

The study of ferrous metallurgical plant slag deserves greater attention as what has already been obtained up to the present moment (through laboratory determinations) makes it possible for us to anticipate that slag can be efficiently used instead of the aggregates obtained from natural rocks.

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