BINDING PROPERTIES OF DIFFERENT TYPES OF IRONMAKING SLAGS[1]

Vsévolod Mymrin[2]
Ronaldo Belinovski Ferreira[3]
Ramon Cortez Paredes[3]
Haroldo Araújo Ponte[3]

Abstract

All the types of dumped ferrous slag (blast furnace, open hearth, electric steel and converter) have manifested unequivocal binding properties. They were studied by wide range of traditional and novel methods self-contained binding properties and physicochemical processes of hydrated slag strengthening up to 6 years of the samples age. The only new crystal formations, detected over a 6-year-long hardening process, were various crystalline carbonates in such small amounts that they cannot be responsible for the materials, highly significant strength (up to 40 MPa) at one year of age. Their long-term properties allow these types of slag to be used as traditional binders, in the preparation of materials for highway, airfield runway, dam and building foundation construction applications. More than 300 km of highways with roadbeds from these materials have shown excellent performance indices in different parts of Russia, including Siberia and Russian North. Now similar research began in Federal University of Paraná with scientific leadership of the first author of this report with some metallurgical slags of Brazilian industry, interested in economically more efficient way of their wastes utilization.

Key words: Dump ferrous slags; Chemical interaction; Strengthening; Construction materials.

PROPRIEDADES LIGANTES DE DIFERENTES TIPOS DE ESCÓRIAS SIDERÚRGICAS

Resumo

Todos os tipos de escórias siderúrgicas (altos-fornos, Siemens-Martin, arco elétrico e conversor) têm manifestado inequívocas propriedades ligantes. Durante 6 anos, amostras de escórias hidratadas foram estudadas por diversos métodos tradicionais e inovadores avaliando as propriedades ligantes e os processos físico-químicos de fortalecimento. As únicas novas formações de cristais detectados durante este período, foram cristais de carbonatos em quantidades tão pequenas que não podem ser significativamente responsáveis pelas propriedades de resistência (até 40 MPa) ao 1 ano de idade. A durabilidade destas propriedades permite a utilização das escórias como ligantes tradicionais em materiais aplicáveis na construção de rodovias, pistas de aeroportos, barragens e de fundações de edifícios. Mais de 300 km de rodovias construídos com sub-bases desses materiais têm demonstrado excelente desempenho em diferentes partes da Rússia, incluindo a Sibéria e a região Norte. Atualmente na Universidade Federal do Paraná, sob liderança científica do autor desse artigo, iniciaram-se estudos utilizando escórias siderúrgicas de indústrias brasileiras interessadas economicamente em métodos eficientes de destinação dos seus resíduos.

Palavras-chave: Escórias siderúrgicas; Interação química; Fortalecimento; Materiais de construção civil.

1 *Technical contribution to the 3rd International Meeting on Ironmaking, September 22 – 26, 2008, São Luís City – Maranhão State – Brazil*
2 *Russian Academy of natural Sciences, Moscow, Rússia – corresponding author. Federal University of Paraná, Centro Politécnico, CEP 81531-990, Curitiba, Brazil.*
3 *Federal University of Paraná, Centro Politécnico, CEP 81531-990, Curitiba, Brazil.*

1 INTRODUCTION

Dump ferrous slag (DFS) is a metallurgical industry waste producing in large amounts and polluting the nature. The international literature contains many reports on multiple ways of metallurgical slag using. The largest consumers of slag in the form of inert material rather than crushed natural stone, gravel and sand mixtures are road constructors.(1,2) Another widespread application of slag is in the production of Portland cement.(3) Technologies of slag-wool production for thermal and acoustic isolation and for technical glasses are well known. Some authors propose the use of slag to coat environmentally hazardous materials,(4) etc. However, most reports so far have concentrated on the use of granulated ferrous slag, a waste product that is not strictly industrial waste but an intermediate product of Portland cement production.

An overwhelming majority of countries that have huge metallurgical industries, however, face a serious problem of what to do with their DFS. All these countries have grave environmental protection problems resulting from the enormous amounts of slag produced, the large areas required to store DFS and the long periods of time over which they have been accumulating. As an example, a single Russian metallurgical plant in Magnitogorsk has accumulated more than 180 million tons of DFS in a nearby dump.

The first author of this paper published(5-7) the results of their investigation into the possibility of chemically strong binding of Electric-Arc Furnace Dust (EAFD) using DFS and of obtaining new construction material. However, no explanation was given of the nature of this slag's binding properties, nor was it reported that practically every type of DFS deriving from metallurgical processes possesses such binding properties, albeit to differing degrees. This paper is dedicated to partially filling in the gaps of our previous publications.

2 RESEARCH GOALS

1. to study the self-contained binding properties of DFS from different metallurgical processes without the addition of any activators;
2. to study the physicochemical processes of hydrated slag strengthening over long periods (up to 6 years of age);
3. to study physicochemical processes of slag strengthening, activated by small (2-3%) of Portland cement and their mechanical properties during hydration over long periods (up to 6 years of age).

3 METHODS OF RESERCH

For the achievement of this goals a wide range of traditional and novel methods of mutually complementary research were used to study the initial slag compositions and their temporal changes during hydration. These methods included the definition of the limit strength under uniaxial compression, temporal changes of moisture and of linear deformation, water and frost resistance, XRD, the quantity of bonded water and carbonate content, using TGA and DTA, SEM and chemical analyses (free CaO, SiO_2, Fe_2O_3, Al_2O_3, SO_3, pH and others), Roentgen-spectral analysis using "Cameca", "Edax" and "Link-System", and Laser micro-mass analysis by "LAMMA-1000". Presenting the results of all these methods here would be impossible owing to space limitations; nonetheless, they have been taken into consideration in the description of the materials strengthening process.

All the types of slag under study were milled to reach the value of specific surface area of approximately 1000 cm^2/g.

4 RESEARCH RESULTS

4.1 Chemical and Mineralogical Compositions of Metallurgical Slag

The chemical and mineralogical compositions of slags variety are very different. For example, $FeO+Fe_2O_3$ contents in the slags are rather high, especially in open hearth slags (till 22%). CaO quantity is very high in converter and blast furnace slags (56-36%). Maximal SiO_2 and SO_3 quantity naturally presents in blast furnace slag (35 and 3.7%).

Table 1. Main components of the chemical compositions (%) of dumped slags under study.

Item	Wastes & Soils	SiO_2	MgO	CaO	Al_2O_3	MnO	$FeO+Fe_2O_3$ Fe2O3	SO_3 common	M_a
1	blast furnace	35.2	3.5	36.1	10.6	2.0	4.0	3.7	0.69
2	open hearth	17.5	18.1	26.7	6.1	2.0	22.1	0.2	1.85
3	converter	19.5	1.8	56.1	2.1	6.7	11.0	0.1	1.57
4	electric steel	18.4	16.5	29.6	10.9	4.2	16.2	0.5	2.67

Where: modulus of alkalinity $M_a = \dfrac{CaO + MgO}{SiO_2 + Al_2O_3}$

Table 2. Mineral compositions of dump ferrous slags.

Minerals of dump ferrous slags	Content in slags, %			
	Blast furnace	Open hearth	Converter	Electric steel
Melilite- $4CaO(Al_2O_3.MgO).3SiO_2$	25 -30	5	-	5
Pseudowollastonite -□-CaO. SiO_2	5	-	-	-
Calcium Silicate-□- $2CaO.SiO_2$	10	-	-	-
Glass	60 -70	5	-	10
Larnite-$2CaO.SiO_2$	-	25	-	40
Olivine-$(Mg,Fe)_2.SiO_4$	-	15	-	-
Magnesia - MgO	-	25	-	20
Rhombic Pyroxene	-	10	-	-
Non transparent phase	-	10	-	-
Ferrites $2CaO.Fe_2O_3$	-	10	15	-
Montichellite - $CaO.MgO.SiO_2$	-	-	-	10
Alite - $3CaO.SiO_2$	-	-	45	-
Belite - □-$2CaO.SiO_2$	-	-	20	-
Braun Mullerite - $4CaO.Al_2O_3.FeO$	-	-	15	-
Free CaO	-	-	2	-
RO-phase - (MgO, MnO, FeO)	-	-	1	-
Magnetite - (Fe_3O_4)	-	-	3	-
Iron	-	-	3	-

The differences in the chemical compositions of all types of slag lead to distinct values of modulus alkalinity, M_a, which is one of the most important indicators of the

binding properties of inorganic materials. Converter slag has the best M_a while blast furnace slag has the worst.
The petrographic and XRD analysis showed that the mineral compositions (Table 2) are differs much more then chemical because of different types of all the input components, temperature regimes of metallurgical technologies, their end-product and dump conditions. The main minerals of dump blast furnace slag are melilite (25-30%), -modification of bicalcium silicate (10%), pseudowollastonite (5%) and glass (60-70%). Another types of dump ferrous slags differed of blast furnace slag and each other very much. The most similar are qualitative mineral compositions of open hearth and electric steel smelting dump slags, but in quantitative compositions they are very far of each other. The most close to the Portland cement mineral composition is converter dump slag, which includes so important Portland cement minerals as alite (45%) and belite (20%). This fact allows to expect the most strong binding properties of converter slag.

4.2 Metallurgical Slags Strengthening without Activation

1. Dump ferrous slags from all the metallurgical processes under study (blast furnace, open-hearth, converter and electric steel) have clearly defined binding properties even without some chemical activation (Figure 1). However, the development of these properties is so slow that only open hearth and converter slags can be used as an independent material without the addition of Portland cement activators.

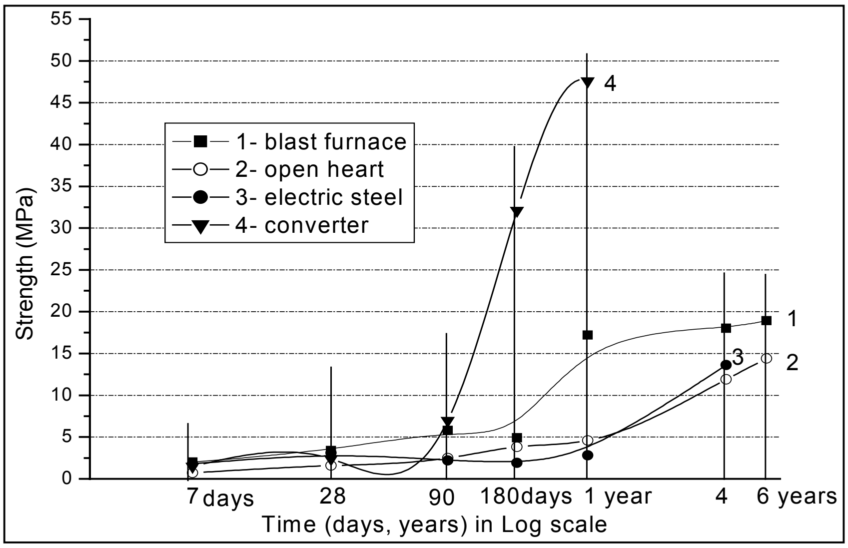

Figure 1. Strengthening of hydrated DFS from different metallurgical processes: 1 – Blast Furnace, 2 – Open Hearth, 3 – Electric Steel, 4 – Converter.

Water and frost resistance properties of DFS hydrated without some chemical activation (Table 3) can be estimated as satisfactory only for open heart and converter slags, and as very low for electric steel slag. All specimens of blast furnace slag are spontaneously destroyed during frost resistance tests.

Table 3. Water and frost resistance coefficients of ferrous slags.

Slag	Rw	Cw	R_f	Cf
Blast furnace	0.39	0.28	0	0
Open hearth	2.69	1.15	2.84	0.96
Electric steel	2.60	1.21	1.51	0.48
Converter	12.22	1.06	9.04	0.74

where:

$C_w = \frac{Rw}{Ra}$ and $C_f = \frac{Rf}{Rw}$;

C_w and C_f - water and frost resistance coefficients of samples;

R_w - strength of 90-day-old samples kept under air-humid conditions (94-96% of humidity)after 24 h saturation in water;

R_a – strength of 90-day-old samples kept under air-humid conditions (94-96% of humidity);

R_f - strength of water saturated sample after 25 cycles of freezing and thawing (-25^{0}C and +20^{0}C in water), each cycle lasting 16 hours.

4.3 Metallurgical Slags Strengthening after Activation by Adding of 2% of Portland Cement

The properties of slag's samples activated by 2% of Portlans cement depend of their chemical compositions. Converter slag of two different plants shows the fastest and most constant increase in strength in hydrated slag samples (Table 4, items 7 and 8), which reach 39.9 and 47.6 MPa at one year of age. This is to be expected in view of this slag's chemical composition, i.e., large amounts of CaO – 56.1 % and relatively small quantities of SiO_2 – 19.5 % and Al_2O_3 – 2.1 %, which result in an M_a = 2.67.

Electric steel slag shows the best strength on the 28th day (3.9 MPa), but the worst (16.2 MPa) in the 6th year. Blast furnace and open-hearth steel slag show very competitive strengths in every stage and display practically the same strength by the end of the 6th year, i.e., close to 20 MPa.

The water and frost resistance of all the types of activated DFS under study are given in Table 4. Russian standard requirements for road base materials from natural soils strengthened with industrial wastes after 90 days of hydration are 6-4 MPa, 4-2 MPa, 2-1 MPa, which correspond to road classes I, II and III. The lowest permissible coefficient of frost-resistance, C_f, of these materials is, respectively, 0.75, 0.70 and 0.65. This means that the strength of water-saturated converter slag, R_w, is far greater (more than double) than the standard's highest requirements. The R_w of open hearth and electric steel slag conforms to class II of the standard, but the frost resistance coefficient, C_f, of the latter falls short of the standard's requirements. Its low water and frost resistance values preclude the use of blast furnace slag without special activation of its binding properties. We have achieved excellent results in terms of activation, to be presented in our next paper.

The results listed in Table 4 confirm our conclusions, based on the values of modulus alkalinity, M_a, in Table 1: converter slag displays the best structural mechanical properties (strength, water and frost resistance), followed by open heart, while blast furnace slag displays the poorest properties.

Table 4. Mechanical properties of activated dump ferrous slags.

Binding materials		Strength (MPa)					Water and Frost Resistance			
		after (days)		after (years)						
Item	Binding	28	90	1	4	6	Rw	Cw	Rf	Cf
1 2	blast furnace	3.4 0.9	5.8 5.1	16.1 14.1	15.0 12.2	20.0 15.4	6.2 4.8	1.1 0.9	5.1 4.6	0.8 1.0
3 4	open hearth	1.6 0.8	2.4 2.5	11.1 4.6	13.8 11.9	19.4 14.4	2.7 2.6	1.2 1.1	2.6 2.1	1.0 0.8
5 6	electric steel	3.1 3.9	2.2 3.0	2.8 10.6	13.67.5	16.49.6	2.6 7.7	1.2 1.1	1.2 6.0	0.5 0.8
7 8	conver- ter	1.6- 2.4	11.6 7.0	17.9 32.1	39.9 47.6	- -	12.2- 3.9	1.1- 0.6	9.0- 5.7	0.7- 1.5

Activation with a 2% content of cement (Table 4) had different effects on different slags, with blast furnace slag showing the most visible improvement in water and frost resistance properties. The results of activation met the highest requirements of the Russian standards.

The least positive results were obtained from the same test on open hearth dump slag, which showed a decrease of all the parameters, particularly of frost resistance. It can, however, be used as an independent material without activation. Open hearth slag contains less SiO_2 and CaO, the two main components in its chemical composition, than the slags deriving from other metallurgical processes (Table 1). Electric steel slag displayed low Cw and Rf, but considerably high Rw and Cf , allowing it to be used as a construction material.

5 PHYSICOCHEMICAL HYDRATED SLAG STRENGTHENING PROCESSES

The hardening processes of all these slags were studied in detail using every possible instrument, as described under the subtitle “Research methods”. Table 5 lists the main physicochemical parameters obtained for blast furnace slag strengthening after hydration. Similar data were also obtained for open hearth, electric steel and converter slag, but are not given here for lack of space.

The data in Table 5 demonstrate that the compression strength of blast furnace slag increases at a slow, variable rate during the first year of hardening, reaching the value of 16.1 MPa. Over the following two years it declines, dropping to 13.6 MPa, but subsequently regains its earlier level and continues increasing until it reaches 20.0 MPa in the 6th year.

Table 5. Changing of the blast furnace slag strengthening indices.

Indices	Time of hardening											
	Days						Years					
	0	7	28	60	90	180	1	2	3	4	5	6
Compression resistance, MPa	-	0. 2	0.5	1.2	1.4	4.2	16.1	14.3	13.6	15.0	17.1	20.0
Coefficient of lineal deformation, %	0	0.31	0.35	0.48	2.04	1.30	1.35	1.74	2.22	2.74	3.04	1.70
CO_2 content, (TG), %	0.25	0.61	0.77	0.92	1.53	1.97	3.91	5.67	6.50	7.60	7.83	7.85
Bonded water losses, (TG), %	2.50	3.63	4.36	3.95	4.06	4.21	5.48	5.38	4.50	5.40	6.17	5.75
pH	8.49	9.15	9.36	9.25	9.29	9.29	9.30	8.41	8.14	8.06	8.00	7.92
Varying SiO_2 unbound content, %	0	0.23	0.30	0.40	0.54	0.76	2.20	4.22	5.00	5.27	5.60	5.81
Varying Al_2O_3 unbound content, %	0	0.17	0.15	0.15	0.14	0.14	0.06	0.17	0.10	0.13	0.15	0.17

The linear deformation coefficient rises in two “waves”, peaking on the 90th day (2.04 %) and in the 5th year (3.04 %), and subsequently dropping to 1.70% in the 6th year.

The constant expansion of CO_2 involves the process by which a sample carbonizes over time. This process, which is more clearly illustrated by the DTA curves, is due to the constant increase of the endothermic effect over time, reaching its extreme at 850°C. The carbonate peak became visible (0.77% of CO_2 upon conversion to $CaCO_3$ is equal to 1.75%) only after 28 days of the material’s hydration. This increase was so slight for the three carbonates (calcite, magnesite and dolomite), that it was almost invisible by XRD.

At first there was endothermic maxim of 780°C resulting from the carbonates’ very low level of crystalline structure formation and the presence of different types of carbonates. The increase in the quantity of carbonates and the perfection of the material’s crystalline structure led to the development of the endothermic effect and caused it to shift to the right on the temperature scale, from 780°C on the 28th day to 850°C at the end of the 6th year. After the first year, the amount of CO_2 (3.91%) was only one half the amount present in the middle of the 6th year (7.85%). The material’s carbonization process gradually slowed down until it almost stopped from the 4th to the 6th year.

The increase in bonded water quantity show three peaks whose maxim occurred on the 28th day and after 1 and 5 years. The loss of resistance between 1 and 4 years and the consequent increase in strength are congruent with the corresponding changes in bonded water quantity in the samples.

The pH value slowly rose from 8.49 up to 1 year (9.30), after which it dropped sharply to 8.41 (lower than initial value), after which it gradually declined to 7.92 in the 6th year.

This increase in alkalinity during first year is attributed to the process of alkaline excitement of the solid surface of slag and the removal of all the chemical elements of the slag’s grains. The alkaline ions (Ca and Mg) of these elements increase the common alkalinity of pore solutions. Some of the Ca and Mg ions are bonded in very different complex compounds of new formations and are partly bonded by the CO_2 of the air present in the carbonates. The process of leaching and removal of ions predominates during this period over the process of alkaline ion bonding and the pH increases.

At the beginning of the hydration process, the density of the pore solution is rather low, but it increases over time. Based on our observations, it appears that after the first year, the density of the new formation around the slag's solid surfaces becomes sufficiently dense to prevent future strong erosion of slag particles by alkaline pore solutions. At this point, the process of alkaline ion adsorption into the complex compounds of new formations predominates over the removal of these ions from the solid slag, and the alkalinity decreases over the second and subsequent years to levels below the original value, continuing to decrease until it reaches pH=7.92.

In our opinion, that is the main reason for the decrease in the aforementioned velocity of these materials' strengthening and carbonization.

The quite considerable density of the new formation gives rise to its process of syneresis, which is well known in colloidal chemistry. One of the main indications of syneresis is the appearance of a network of specific cracks. Such cracks are highly visible in the bodies of the slag's new formation at 180 days and 6 years. Due to this syneresis-related cracking, the liquid phase of alkaline pore solutions approaches the surface of solid slag particles and begins to leach out.

SEM micrographs depict the transition of separate particles from the original slag to the new formation over 28 days, showing rounded shapes devoid of crystal-like bodies. At 180 days these rounded shapes are covered with a network of rather deep syneresis-related cracks. These cracks are subsequently sealed by the generation of fresh amorphous gel formations.

Table 6. Typical chemical composition on X-ray-spectral analysis using "Link-System" of the nearest points of new formations of Blast Furnace Slag after 28 days of hydration.

Points	Elements, %					
	Mg	Al	Si	Ca	Mn	Fe
A	5.58	23.17	18.24	51.70	0.07	1.24
B	0.77	13.28	2.43	69.81	0.81	2.90
C	1.19	16.32	47.24	34.15	0.90	0.20
D	0.10	5.77	81.24	12.43	0.02	0.44
E	0.97	7.01	14.17	62.29	1.29	4.27
F	0.24	5.44	73.18	8.21	0.81	2.12

The filling of their trenches by amorphous materials and the appearance of parapet-like shapes on both their sides evidence this crack sealing effect.

The amorphous nature of new formation is confirmed by:

1. The absence of new peaks on the XRD up to the samples' age of 6 years, with the exception of the carbonates;
2. The aforementioned absence of crystal-like shapes revealed by SEM, the presence of specific syneresis-related cracks and their sealing over time by new coatings of gel;
3. The presence of wide exothermic areas, varying from 180°C to 750°C, on the DTA curves of all ages;
4. The results of roentgen-spectral analysis using "Cameca", "Edax" and "Link-System", Table 6. Chemical compositions of all most close points of new formations were quite different;
5. The results of laser micro-mass analysis, similar to results of Laser micro-mass analysis by "LAMMA-1000". All the spectra obtained for the chemical compositions

of all the nearest points of new formations show quite dissimilar combinations of isotopes and its quantities (intensity).

6 RESULTS APPLICATION

Some of the applications resulting from this research work were used in the construction of almost 300 km of roadbed in different parts of forma URSS, from semi desert hot regions of Uzbekistan including the central regions of Siberia and northern Russia, which have extremely severe climatic conditions. DFS under study of various metallurgical processes were used as binder materials for the strengthening of exceedingly different natural soils as road bases. These roads with different technical categories demonstrated during 20 years or more excellent exploitation properties.

7 CONCLUSIONS

1. Dump ferrous slags from all the metallurgical processes under study (blast furnace, open-hearth, converter and electric steel) have clearly defined binding properties. However, the development of these properties is so slow that only open hearth slag can be used as an independent material without the addition of Portland cement activators.
2. The binding properties of slag can be accelerated easily by the addition of 2% of Portland cement.
3. The strengthening process of all the types of ferrous slags under study is triggered by the synthesis of new amorphous formations. Very small amounts of carbonates are formed as crystal structures, but they cannot be the cause of the samples' strengthening up to 47 MPa at one year of age.

REFERENCES

1 LEE, A.R. Blast furnace and steel slag. Production, properties and uses. London: Edward Arnold Publishers LTD, 1974, p. 119.

2 ROEDERER,C.; GOURTSOYANNIS, L. Steel-Environment. In: Report EUR 16955 EN, Brussel, 1996, pp. 7.17-7.18.

3 ZIVICA V. Admixture for Cement Composites Incorporating Pozzolan or Blast Furnace Slag. Alkalisilicate Cement and Concrete Res 23, 5, 1993, pp. 1215-1222.

4 LOPEZ, F.A.; SAINZ, E.;FORMOSO, A. Use of Granulated Blast-Furnace Slag for Stabilization of Steelmaking Flue Dust. Ironmaking and Steelmaking, v. 20, No. 4, 1993, pp. 293-297.

5 MYMRIN, V.A; VAAMONDE, A.J.V. Construction materials from byproduct ferrous slag and electric arc furnace dust Steel World. 5, 1, 1999, pp. 33-36.

6 MYMRIN, V.A. Waste materials reuse for producing of new highly efficient construction materials *Proc. 3rd Int Cong. on Environmental Geotechnics*, 1998, Lisboa, Portugal, pp.615-619.

7 MYMRIN, V. A. Empleo de residuos industriales siderúrgicos como materiales aglomerantes en construcción. Revista de Metalurgía, 34. 1998, Madrid, pp.441-445.