

ATIVACÃO DAS PROPRIEDADES DE LIGAÇÃO DA ESCÓRIA SIDERÚRGICA PELA ADIÇÃO DE RESÍDUOS DA PRODUÇÃO DE CAL

BLAST FURNACE SLAG BINDER PROPERTIES ACTIVATION BY LIME PRODUCTION WASTE

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Resumo

A escória siderúrgica estudada nesta pesquisa mostrou propriedades de ligação. Esta foi ativada por trituração ou se acrescentando resíduos da produção de cal. A eficiência de ativação da escória triturada ou misturada com resíduos da produção de cal foi comparada a da escória com granulometria ≥ 3 mm. A eficiência de ativação da escória triturada foi observada durante 90 dias e da não triturada durante 6 anos. A resistência uniaxial dos materiais depois de 90 dias variou de 0,83 até 5,07 MPa, depois de um ano aumentou entre 7,46 e 16,00 MPa e depois de 6 anos de 12,48 a 20,40 MPa. O ganho de resistência da escória refere-se à presença de novas formações amorfas, que as transformaram em um material similar à uma rocha. As novas formações cristalinas, observadas no processo enrijecimento após 6 anos, foram carbonatos cristalinos diversos, mas em pequenas quantidades, o que não deve justificar o ganho significativo de resistência observado pelos materiais. As propriedades a longo prazo adquiridas pela escória siderúrgica faz com que este tipo de material possa vir a ser utilizada na construção civil por apresentar resistência de ligação similar ao concreto ou outros materiais de construção.

Palavras-chave: Escória siderúrgica. Influência de fração. Fortificação. Novas formações amorfas. Propriedades dos materiais de construção.

Abstract

Blast furnace slag under study has manifested unequivocal binding properties. They were activated by grinding and by adding of lime production waste and compared with ungrounded fraction \geq

3mm. The activation efficiency of grinded slag was observed only during the first 90 days and of ungrounded slag – during 6 years. Uniaxial resistance strength of the materials on the 90th days varied from 0.83 till 5.07 MPa, during one year it increased till 7.46 – 16.00 MPa and during 6 years – till 12.48 – 20.40 MPa. The strengthening of the slag is ascribed to the appearance of new amorphous formations, which transform into a stone-like condition over time. 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. Their long-term properties allow these types of slag to be used as concrete-like or binder construction materials.

Keywords: Blast ferrous slag. Fraction influence. Strengthening. Amorphous new formations. Construction materials properties.

1 Introduction

The international literature contains many reports on multiple ways of ferrous metallurgical slag using, including blast furnace slag (BFS). The largest consumers of slag in the form of inert material rather than crushed natural stone, gravel and sand mixtures are road constructors (STELL, 1997; ROEDERE; GOURTSOYANNIS, 1996; UNEP; IISI, 1997). Another widespread application of slag is in the production of Portland cement (LEE, 1974). 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 (LOPEZ; SAINZ; FORMOSO, 1993), etc. However, most reports so far have concentrated on the use of granulated ferrous slag 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 ferrous slag. All these countries have grave environmental protection problems resulting from the enormous amounts of slag produced, the large areas required to store slag 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 slag in a nearby dump.

This paper is dedicated to investigation of BFS self-binder properties and their alkaline activation by small (2%) additions of lime production waste (LPW) and to study of new material structure formation processes.

The research goals:

- a) to study the self-contained binding properties of BFS without addition of any activators and with alkaline activation by 2 % of LPW;
- b) to study the physicochemical processes of hydrated slag strengthening over long periods (e.g., up to 6 years of age);

c) to clarify the influence of self-decomposition fractions on the BFS strengthening processes.

2 Research methods and samples preparing

For the achievement of these goals and to study the initial slag compositions it was used some mutually complementary research methods. 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 analyses by the powder method, the quantity of bonded water and carbonate content, using TGA and DTA, EDS and Laser micro-mass analysis by “LAMMA-1000”.

It was studied three fractions of BFS: no separated slag (total), fraction > 3 mm and fraction < 3 mm. Total slag and its fraction > 3 mm were milled to reach the value of specific surface area of approximately 1000 cm²/g, fraction < 3 mm was not milled. The samples of the materials were compacted under a 10 MPa pressure in a cylindrical mold with a 5 cm diameter and height under conditions of optimal humidity (10-12 %). The hardening occurred under a condition of almost 98 % humidity.

3 Raw materials description

Chemical compositions of the BFS fractions (Table 1) have the mainly difference in CaO, MnO and FeO⁺ Fe₂O₃ contents.

Table 1 – Chemical composition of BSF and its fractions

BFS and its fractions	Chemical elements contains, wt. %								
	SiO ₂	MgO	CaO	Al ₂ O ₃	MnO	FeO ⁺ Fe ₂ O ₃	SO ₃	TiO ₂	C.L.
Total	35.2	3.5	36.1	19.6	2.0	4.0	3.7	0.9	0.9
Fraction > 3mm	36.8	3.3	40.4	19.6	2.4	0.4	4.1	0.4	0
Fraction < 3mm	37.1	3.7	35.4	9.6	0	6.6	3.6	0	2.0

Source: Author

Mineralogical composition of total BFS, studied by petrography method of oily liquids immersion, was the next: Melilite (25-30 %), α -C₂S (10 %), glass (60-70 %). The composition of the fraction < 3 mm is rather differed of total BFS: Melilite (25-30 %), α -C₂S (30-40 %), CaSO₄ (20%) and CaCO₃ (20 %).

Density of the total slag was 2.98 g/cm³, of their fraction > 3mm, 3.04 gr/cm³, and of fraction < 3mm, 3.17 g/cm³, possibly because of difference in metal oxides content; humidity level varied between 0.44 and 0.92 %. Total slag and fraction > 3 mm were grounded till 1000 cm²/g. To

clarify the binder properties of self-decomposition fraction < 3 mm it was not grounded and it had specific surface 300 cm²/g.

Chemical composition of LPW contains 48.41 % of CaO, 25.18 % of MgO, 1.89 % of SiO₂, 0.23 % of Fe₂O₃ and 0.19 % of Al₂O₃. High calcinations lost (24.07 %) of dried LPW with zero quantity of SO₃ and P₂O₅ can be explained mainly by CO₂ lost of raw carbonates insufficient roasted. In accordance with Brazilian norm NBR 6453 (ABNT, 2003) calcinations lost of construction lime must be no more than 12%. Lime with exceeded value must be classified as lime production waste (LPW). Usually it used for acid soils neutralization; Mymrin and Correa (2005) used it for concrete waste and debris utilization to produce new construction materials.

4 Experimental results discussion

Hydrated and compacted BFS and its fraction quite clearly show their binder properties even without some activators (Table 2, items 1, 3 and 5), but usually it is going on very slowly, only on the 90th day and became more visible on the 180th day of hydration.

Table 2 – Comparison of uniaxial resistance changes of no activated BFS and activated by 2% of LPW

n°	Fraction of slag	LWP as activator, wt. %	Resistance (MPa) on days/years of strengthening						
			days				years		
			7	28	90	180	1	3	6
1	Total BFS, grounded	0	0.18	0.51	1.40	4.22	16.00	13.59	20.40
2		2	0.35	0.87	5.07	4.07	14.12	10.95	15.41
3	Fraction > 3 mm, grounded	0	0.09	0.38	0.83	1.98	7.46	15.15	13.20
4		2	0.21	0.69	3.79	4.06	13.52	7.036	12.48
5	Fraction > 3 mm, no grounded	0	0.07	0.15	1.53	4.35	6.38	9.27	12.87
6		2	0.19	0.34	5.47	8.80	9.29	6.52	10.18

Source: Author

Alkali activation of BFS and its fractions by 2 % of LPW (Table 2, items 2, 4 and 6) increased their 90th day resistance in 3-5 times, but only during rather limited time. Resistance strength of no activated total BFS is higher than activated already on the 180th day. The same effect is visible with both fractions on the 3rd year.

The growth of resistance values of all materials under study is not going on rectilinearly, but with temporary decreasing and new increasing, especially on the 3rd year.

The water and frost resistance of all the types of DFS under study are given in Table 3.

Table 3 – Comparison of water and frost resistance of no activated and activated by 2 % of LPW materials (Equation 1)

Indices	Hardening time											
	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	20.4
Coefficient of lineal deformation, %	0	0.25	0.31	0.64	1.90	1.57	1.28	1.62	2.08	2.63	2.78	1.94
Common weight losses, (TG), %	2.63	3.44	4.30	4.63	5.92	6.27	9.07	10.8	11.2	13.4	14.2	13.2
CO ₂ content, (TG), %	0.20	0.47	0.69	0.90	1.34	1.82	3.47	5.29	6.11	7.38	7.69	7.73
Bonded water losses, (TG), %	2.43	1.97	3.61	3.73	4.58	4.45	5.60	5.51	5.09	6.02	6.51	5.47
pH	8.35	9.33	9.43	9.18	9.19	9.18	9.32	8.48	8.11	8.02	7.95	7.82

Source: Author

where:

$$C_w = \frac{R_w}{R_a} \text{ and } C_f = \frac{R_f}{R_w} \quad (1)$$

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

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

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

R_f – strength of water saturated sample after 25 cycles of freezing and thawing (-250 °C and +250 °C in water), each cycle lasting 16 hours.

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 its low water and frost resistance values preclude the use of BFS without special activation of its binding properties. Small (2 %) addition of LPW increase water resistance R_w value of total BFS in more than 12 times (Table 3, items 1 and 2) and coefficient of water resistance C_w value till 0.94. The both indices are corresponding to road base material of class I.

Similar efficiency of both BFS fractions by 2 % of LPW

The coefficient of water resistance values of activated total BFS and the both of its fractions C_w are 0.94 – 1.17 and 0.98 respectively. Its 90-days water resistance values (5.07 – 3.79 – 5.47 MPa, Table 2) are very close to highest standard's resistance requirements (6.0 MPa). The same is observed with values (0.96 – 0.77 – 0.82) of frost resistance coefficients C_f of BFS and fractions samples (the highest standard demand is 0.75).

The results listed in Tables 2 and 3 confirm the conclusion that total BFS slag displays the best structural mechanical properties (strength, water and frost resistance) in comparison with its fractions.

5 Physicochemical hydrated slag strengthening processes (illustrated with blast furnace slag)

List of some physicochemical parameters obtained for total BFS activated by 2% LPW is presented in the Table 4. It demonstrates that the compression strength 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 20.4 MPa in the 6th year.

The linear deformation coefficient rises in two “waves”, peaking on the 90th day (1.90 %) and in the 5th year (2.78 %), and subsequently dropping to 1.94 % in the 6th year.

The weight loss commonly occurring during heating to 1000 °C consists of CO₂ content and bonded water.

Table 4 – Changing of the blast furnace slag strengthening indices

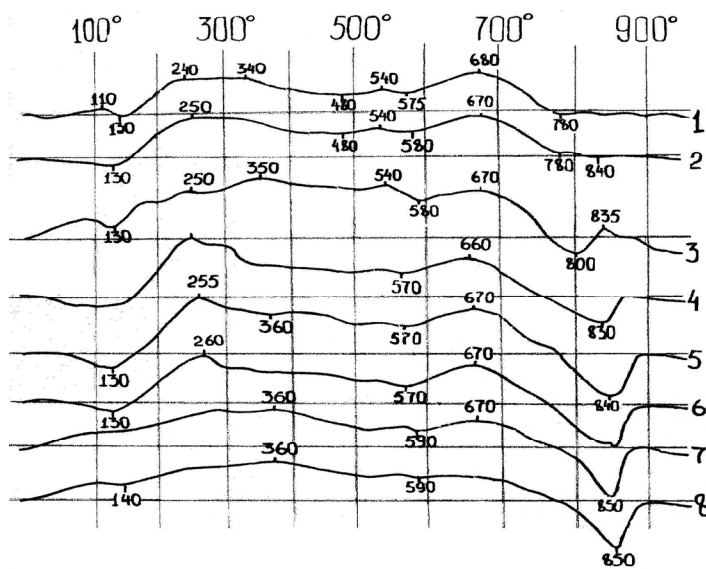
Indices	Hardening time											
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Compression resistance, MPa	-	0.2	0.5	1.2	1.4	4.2	16.1	14.3	13.6	15.0	17.1	20.4
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Source: Author

The constant expansion of CO₂ involves the process by which a sample carbonizes over time. This process, which is more clearly illustrated by the DTA curves (Figure 1), is due to the constant increase of the endothermic effect over time, reaching its extreme at 850 °C (Fig. 1, curve 8). Initial BFS contains 0.20 % of CO₂, upon conversion to CaCO₃ is equal to 0.45 %, practically

invisible on DTA curve. The carbonate peak became visible (0.69% of CO₂ upon conversion to CaCO₃ is equal to 1.57 %) 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. But after the first year, the amount of CO₂ increased till 3.47% or CaCO₃ = 7.89 % and to the 6th year increased till 7.73 % of CO₂, equal to 17.57 % CaCO₃. Thus CaCO₃ content was increased during 6 years of the BFS hydration from 0.45 till 17.57 %. The material's carbonization process gradually slowed down until it almost stopped from the 4th to the 6th year.

Figure 1 – Changes in DTA curves during inactivated BFS strengthening after hydration for 7 days (1) , 28 - (2), 90 - (3), 2 years - (4), 3 years - (5), 4 years - (6), 5 years - (7), and 6 years - (8)



Source: Author

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 carbonates 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.

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. It well visible also wide area of exothermic peak from 180 °C till 750 °C of amorphous new formations, which are indicated by XRD due to high background of their diffractograms.

The pH value (Table 4) 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 CO₂ 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.

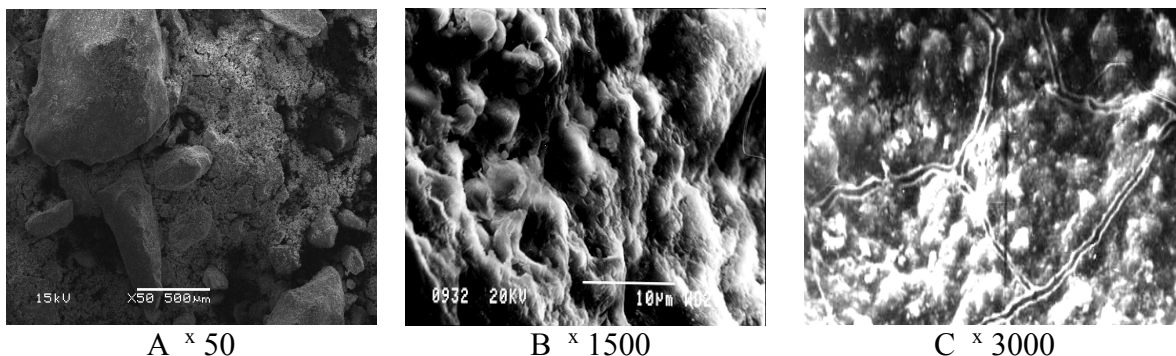
At the beginning of the hydration process, the density of the pore solution is rather low, but it increases over time. Based on our observations, it appears that after the first year, the density of the new formation around the slag's solid surfaces becomes sufficiently dense to prevent future strong 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 (Figure 2C) 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 (Figure 2) depict the transition of separate particles from the original slag (Figure 2A) to the new formation over 28 days, showing rounded shapes devoid of crystal-like bodies (Figure 2B). At 180 days (Figure 2C), 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.

Figure 2. SEM image of activated Blast Furnace Slag: A – before the hydration, B – after 28 days, C – 180 days, D – 6 years of hydration



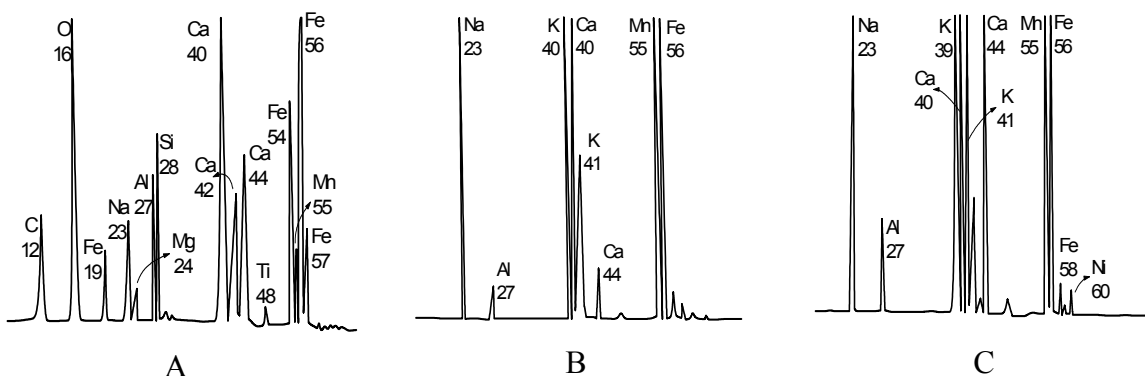
Source: Author

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:

- The absence of new peaks on the XRD up to the samples' age of 6 years, with the exception of small quantities of the carbonates;
- 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;
- The presence of wide exothermic areas, varying from 180 °C to 750 °C, on the DTA curves of all ages;
- The results of laser micro-mass analysis, similar to results of Laser micro-mass analysis by "LAMMA-1000", Fig. 3. 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).

Figure 3 – Typical Laser Micro-Mass Analytic (LAMMA) specters A, B and C of new formations on the 60th day of BFS hydration



Source: Author

6 Conclusions

- It was experimentally proved that blast furnace slag and its fraction > 3 mm and < 3 mm manifested self-binding properties.
- These properties can be increased by mechanical desperation of slag and by adding of lime production waste. The activation efficiency of grinded slag was observed only during the first 90 days and of ungrounded slag – during 2 years. Uniaxial resistance strength of the materials on the 90th days varied from 0.83 till 5.07 MPa, during one year it increased till 7.46 – 16.00 MPa and during 6 years – till 12.48 – 20.40 MPa.
- The strengthening of the slag is ascribed to the appearance of new amorphous formations, which transform into a stone-like condition over time. 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. Their long-term properties allow these types of slag to be used as concrete-like or binder construction materials.

- d) The wide-scale using of the method is environmentally effective, because the most important advantage of this method are utilizing of industrial wastes that contaminates the environment and reduces open-quarry extraction of natural construction materials.

References

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 6453**: cal virgem para a construção civil: requisitos. Rio de Janeiro, 2003.

LEE, A.R. **Blast furnace and steel slag**: production, properties and uses. London: Edward Arnold Publishers LTD, 1974, 132 p.

LOPEZ, F.A.; SAINZ, E; FORMOSO, A. Use of granulated blast-furnace slag for stabilization of steelmaking flue dust. **Ironmaking and Steelmaking**, v.20, n.4, 1993, p. 293-297, 1993.

ROEDERE, C.; GOURTSOYANNIS, L. **Technical steel research**: coordinate study "steel environment". Luxemburg, 1996. 430 p. Disponível em:
<<http://www.google.com.br/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0CCEQFjAA&url=http%3A%2F>>. Acesso em: 10 jun 2014

STEEL for sustainable development. In: ENCOSTEEL CONFERENCE, 1997, Estocolmo. **Proceedings...** Bruxelas: International Iron and Steel Institute, 1997.

UNITED NATIONS ENVIRONMENT PROGRAMME (UNEP) AND STEEL INSTITUTE (IISI), 1997. **Steel industry and the environment: technical and management issues**. Technical Report No. 38. Paris: UNEP; Bruxelas: IISI, 1997.