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ISSN 0543-5846
METABK 45 (3) 163-168 (2006)
UDC - UDK 669.162.275.2+669.186.58=111

UTILIZATION OF IRONMAKING AND STEELMAKING SLAGS

Received - Primljeno: 2005-10-21
Accepted - Prihvaćeno: 2006-03-25
Review Paper - Pregledni rad

The paper deals with the most important processes used for treatment of blast furnace and steelmaking slags and with the most important ways of their utilization. The method of recycling of steelmaking slags that followed from the experiments of the authors, are described. Proposal for the way of utilization of one sort of ladle furnace slag is also included.

Key words: *blast furnace slag, steelmaking slag, utilization, recycling*

Korištenje visokopećnih i čeličanskih troski. Rad se bavi najvažnijim procesima tretiranja viskopećne troske i troske iz čeličana te najvažnijim načinima njihovog korištenja. Opisana je metoda recikliranja troske iz čeličana koju je autor koristio u svojim eksperimentalnim radovima. Također je uključen i prijedlog za način korištenja jedne vrste troske iz metalurškog lonca.

Ključne riječi: *visokopećna troska, čeličanska troska, korištenje, recikliranje*

INTRODUCTION

Smelting of hammerable iron and its treatment in Antiquity and Medieval produced also by-product: slag. Because of small yields of iron the process produced only small amounts of slag that did not attract attention of smelters concerning its possible use. The use of slag pieces was only accidental. A lot of slag pieces and blocks from slag pit shaft furnaces were used as a material for mound building around a church in central Denmark. The author of this paper found pieces of smithy slag in walls of houses in medieval town Cencelle in Italy [1]. In some cases rich sources of iron smelting slags were used by modern smelters. Thick layers of iron-rich smelting slags, by-products of Etruscan iron smelting in Populonia, were extensively used as an iron source by 2nd world war Italian metallurgy.

The introduction of charcoal blast furnaces in the 16th century in west Europe is also a starting point in regular utilization of metallurgical slags, mainly blast furnace slags. Though the first use of blast furnace slag was in road construction, within a short time it acquired the name "material for many ways of utilization". In the 20th century many institutions and societies appeared with the main aim to support the use of full production of both ironmaking and steelmaking slags. In present the utilization of the slags is the measure of level attained by steel metallurgy in the country or region.

In this paper some remarks on ways of ironmaking and steelmaking slags utilization are presented. Paragraphs related to steelmaking slags are restricted to slags from oxygen converter refining, from electric arc furnace processes and from ladle furnace processes. The slags from other steelmaking processes, from tundish of continuous caster and from pig iron treatment processes are not included in this paper.

BLAST FURNACE SLAG

Besides pig iron blast furnace produces two important by-products, blast furnace slag and top gas (blast furnace gas), that are fully utilized. The slag is composed of gangue minerals from iron bearing materials, slag forming additions and coke ash. The slag is tapped from the blast furnace together with pig iron at temperatures about 1540 °C.

All structural components of blast furnace slag can be sorted in three general groups [2]:

1. pyroxenes $MeO\times SiO_2$;
2. olivines $2MeO\times SiO_2$;
3. group of gehlenite and melilite $mMeOxnAl_2O_3\ p\cdot SiO_2$.

For treatment and utilization of blast furnace slag its chemical composition and mineralogic structure are decisive. The most important points are:

- character of major mineralogic components,
- crystallization rate,

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- dimensions and forms of crystals.
- occurrence of glassy phase.
- special distribution of crystalline and glassy phases.

According to these points methods of blast furnace slag treatment can be subdivided into three groups [3]:
- slag pit process,
- slag granulation process,
- other processes.

Slag pit process

The slag pit process involves pouring of molten iron into slag pit where slag develops crystalline structure by process of controlled cooling. The slag pit can be constructed adjacent to the blast furnace or be in an other remote place. In the second case slag ladles are used for molten slag transport. Cooling time in the pit is controlled by spraying the hot slag with a controlled amount of water. Recommended amount of sprayed water is 0,2 to 0,4 m^3 of water per m^2 of slag layer area per hour.

After finishing the solidification and cooling the slag is excavated, crushed and sorted according to different sizes of aggregate pieces. The aggregate (blast furnace slag gravel) is used mostly in building of roads and highways (lower layers), in civil engineering, in construction of railway tracks banks, in field arrangements, recultivation, etc. The slag after solidification has bubble-like structure with many disconnected cells. It crushes to angular, cube-like pieces with minimum of flat fragments. Coarse cell-like structure results in bigger surface area than natural gravel. Bigger surface area is favourable for soakability with water.

Chemical composition of the slag aggregates (in wt. %): CaO = max. 40; MgO = max. 16; SiO_2 = min. 35; Al_2O_3 = min. 6; FeO = max. 3; S_{total} = max. 1.

Advantages against natural gravel:
- lower costs of production,
- better heat conductivity,
- absence of organic matters,
- environmental aspects.

Blast furnace gravel is sold in many categories, according to production scheme of the producer and needs of the customer. Two examples: 1. Coarse blast furnace gravel for building purposes - size categories 0 - 8 mm; 0 - 32 mm; 0 - 90 mm. 2. Blast furnace gravel for civil engineering purposes - size categories 8 - 16 mm; 16 - 32 mm; 32 - 63 mm; 63 - 125 mm. Apparent density: 1200 - 1400 kg/m^3; volume density: 2200 - 2700 kg/m^3.

Present standards do not differ between blast furnace gravel and natural gravel. The gravels for different purposes have to reach quality indicators set by standards, e.g. oversized, undersized in %; heterogeneous particles in %; durability; frost-proof properties; soakability; disintegration, etc. From blast furnace gravel point of view the problems lay in low contents of small sizes, silicate disintegration effect, increase of size by binding after long storage.

Slag granulation process

The process involves pouring the molten slag through a high pressure water spray in a granulation device [3]. In most cases the device is built in close proximity to the blast furnace to avoid decrease of molten slag temperature prior to granulation. Then the slag fell down to a water basin and after collection it is dewatered. Final water content of the slag sand (granulated) is about 10 %.

Main field of granulated slag application is in cement production. Besides it the slag sand is utilized in lower layers of roads, highways, pavements, runways, parking places, foundations of buildings, pillars, walls. The slag sand has excellent binding properties and loading limits increase with time. The slag sand is used also for production of concrete pieces, usually in mix with the slag gravel. Fine slag sand can be also used for conditioning of acidic soils.

In production of cement the slag sand can be used either in production of clinker (instead of natural raw materials) or as an addition in production of cement (production of slag-portland cement). From 2000 to 2003 blast furnace slag production increased by 5,0 % p.a. to 200 Mta. In the same period granulated blast furnace slag production increased by 6,7 %, resulting in more than 50 % blast furnace slag granulated today [4].

Apparent density of granulated blast furnace slag: 1100 - 1300 kg/m^3.

Suitability of the slag sand for cement applications is expressed by its hydraulic properties, by index of hydraulicity

$$ih = \frac{\mathrm{CaO} + 1,4\mathrm{MgO} + \mathrm{Al_2O_3}}{\mathrm{SiO_2}}.$$

As can be seen from the formula, for improvement of hydraulic properties of granulated blast furnace slags higher contents of alumina and magnesia are recommended. It can be done by changes in blast furnace charge composition, i.e. increase of alumina constituents and decrease of silica ones.

Mixture of fine grinded granulated blast furnace slag, steelmaking slag and activators of slag hydratation can be used as substitute for cement in application for lower layers of roads. By use of substitute prolonged solidification of the building mixture is achieved. Demanded properties are attained by fine grinding of slag mixture with free lime. Solidification with the slag binder is characterized by continuous increase of strength. The strength of building mixture with use of the slag binder is after 60 days

the same as the strength of mixture with cement after 28 days. The results of the slag binder use are:
- longer durability of road,
- decrease of cracks occurrence,
- lower cost,
- savings in asphalt mixtures.

Other processes

Here are brief remarks on some other applications of the blast furnace slag.

Pelletized slag. It is produced by the modification of granulation process. Molten slag is spread in a layer on a plate called deflector. The layer of slag is torn to pieces by water jets and then the pieces are projected centrifugaly into the air with the help of rotating drum equipped with grooves. Water vapour inside the pieces pushes to cooled outer layer and forms the pellet - like pieces.

***Granulated blast furnace slag sand* [5].** NKK of Japan treats granulated slag by light crushing to produce particles of a uniform size and shape. A consolidation inhibitor is added resulting in fine concrete aggregate.

Expanded blast furnace slag. Expanded slag has crystalline structure. Molten slag is poured into shallow pits (about 30 cm depth) with bottom equipped with set of water jets. Determined amount of water injected into the molten slag evaporates and forms bubbles, channels and voids of different shape in slag during cooling and solidification. The slag after solidification is excavated, crushed and sorted. The expanded slag gravel is used for production of light concrete pieces. Such pieces posses light weight, high durability, high strength and high temperature resistance properties. Because of excellent binding properties expanded slag is utilized in construction of walls, dams, wharfs. Apparent density of expanded slag is 800 - 1040 kg/m^3.

Technical ceramics. Most types of technical ceramics are rather expensive because of expensive raw materials (Li_2O, B_2O_3, TiO_2) used for their production. Some types of glassceramics can be prepared from industrial wastes, mostly from metallurgical slags. To convert the basic slag to the crystalline - glassy material with needed properties, it is necessary to change its composition by addition of silica sand and some other materials [6, 7]. A mixture for smelting contains 50 to 65 % of blast furnace slag, 20 to 40 % of silica sand, up to 12 % of clay, 4 to 6 % of Na_2SO_4, 1 to 3 % of C, 0.5 to 2 % of nucleators. Final composition of slagsital is 52 - 62 % SiO_2; 5 - 15 % Al_2O_3; 22 - 28 % CaO; 1 - 7 % MgO; 4 - 8 % Na_2O + K_2O. As nucleators MnS + FeS; TiO_2 + P_2O_5; Cr_2O_3 + MgO are preferably used. The slagsitals are used mostly for production of facings in civil engineering, in building of industrial halls, shops, etc. Their most interesting properties are:
- high strength,
- resistance to abrasion,
- temperature resistance up to 900 °C,
- resistance to acidic and basic conditions.

Filtration medium for waste (mainly industrial) water. Applicable mainly in severe climatic conditions with abrupt changes of very cold and very hot weather.

STEELMAKING SLAGS

Steelmaking slags from refining processes both in oxygen converter and in electric arc furnace contain a high portion of refined metallic iron - raw steel. The first and very important process of steelmaking slag treatment is to divide the slag into two parts: a metallic one (steel scrap); and a demetallized steelmaking slag. Multistep process of crushing, grinding and electromagnetic separation is utilized for this purpose.

Demetallized part of steelmaking slag is utilized in civil engineering, in roads, dams, moles etc. construction. It is used mainly for stabilization of lower parts of soil because of high specific density of steelmaking slag. Applications in cement production industry and in treatment of acidic soils are also well - known.

The main obstacle for utilization of steelmaking slag in roads construction and similar applications is it's prone to self - degradation, caused by presence of free lime in the slag and its hydratation ability accompanied by volume changes. The most similar method how to overcome this obstacle is natural ageing of the demetallized slag at an outdoor yard. The process takes 6 to 9 months.To shorten the time of ageing a few processes were developed in Japan, Germany and Brazil [8]:
- ageing by water steam,
- ageing by water steam under pressure,
- ageing by silica sand injection into liquid steelmaking slag,
- ageing by hydratation and aeration - ACERITA process.

Very important way of utilization of steelmaking slag is its recycling into blast furnace or steelmaking unit charge. The authors of this paper performed in previous years a lot of plant experiments with recycling of steelmaking slag.

Recycling of oxygen converterslag into sinter and blast furnace charge

Team of research workers from East Slovak Steelworks and Technical University in Košice [9] introduced in the second half of the eighties a new method for self - disintegration of oxygen converter slag and its utilization in sinter and blast furnace charge. During tapping of slag from converter into a slag ladle (about 15 tons of slag put into the ladle) 300 kg of crushed limestone was added. After solidification of slag in the ladle and following dumping in the slag yard most of the slag existed in disintegrated form, Figure 1. Next the slag was sorted to three categories: 0 to 5 mm; 5 to 50 mm; and oversized. The category 0 to 5 mm

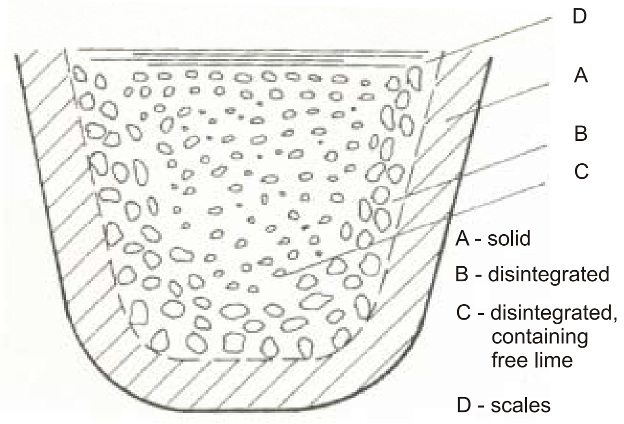

Figure 1. **Disintegration of steelmaking slag after addition of crushed limestone into slag ladle**
Slika 1. **Razlaganje čeličanske troske nakon dodavanja usitnjenog vapnenca u lonac s troskom**

was put into the sinter charge and category 5 to 50 mm into the blast furnace charge. The slag could substitute a part of limestone, dolomite and manganese ore in the sinter charge and a part of limestone and dolomite in the blast furnace charge. Disadvantages of the method were:

- decrease of iron content in both sinter and blast furnace charge,
- increase of phosphorus contents in both types of charges.

The method was used in practice up to 1995 when a new way of steelmaking slag treatment started.

Recycling of oxygen converter slag into oxygen converter charge [10]

Recycled slag in refining process in oxygen converter can serve as an initiator of slag formation, as a medium providing start of lime solution at the beginning of refining process. Recycled demetallized slag can decrease costs of slag forming additions (lime).

Major structural components of demetallized slag are dicalcium silicate, tricalcium silicate, RO-phase, calcium ferrites, free lime. All of them are components of final slag from oxygen converter. Phoshorus in slag is combined with dicalcium silicate in form of solid solution $2CaO{\cdot}SiO_2$ - $3CaO{\cdot}P_2O_5$, sulphur as CaS is combined with calcium ferrites as Ca - S ferrite. As demetallized slag contains both dicalcium silicate and calcium ferrites, both desulphuration and dephosphoration processes can start from the beginning of the refining process.

Sets of experiments were performed at steel plants of East Slovak Steelworks in Košice. In the first part of experiments additions of 1000 kg, 2000 kg, 3000 kg and 4000 kg of demetallized slag were charged into 180 t oxygen converter, total 25 heats with recycling of demetallized slag were realized. Recycling of the slag was realized in different parts of refining process. The second part of experiments contained 12 heats in the same converter. The first three heats were produced without recycling of demetallized slag, next three heats with 1000 kg of demetallized slag, the last six heats with additions of 4000 kg of demetallized slag. Three of them were prepared with decreased amount of charged lime (– 2000 kg). In the third part of experiments a statistic set of 17653 heats, that contained the heats without recycling of demetallized slag, the heats with additions of up to 2000 kg of demetallized slag, the heats with additions more than 2000 kg of demetallized slag were studied. The results of the experiments are:

1. Negative influence of demetallized slag recycling on refining process parameters, mainly desulphuration and dephosphoration processes, was not found, Figure 2.
2. Reality of substitution of part of charged lime was documented. Substitution ratio lime - demetallized slag 1:2 was proposed.
3. Recycling of demetallized slag had only small effect on chemical composition of converter slag.
4. Free lime contents in slags decreased with increased amount of recycled demetallized slag.
5. Recycling rate of demetallized slag up to 25 kg per ton of raw steel is recommended.

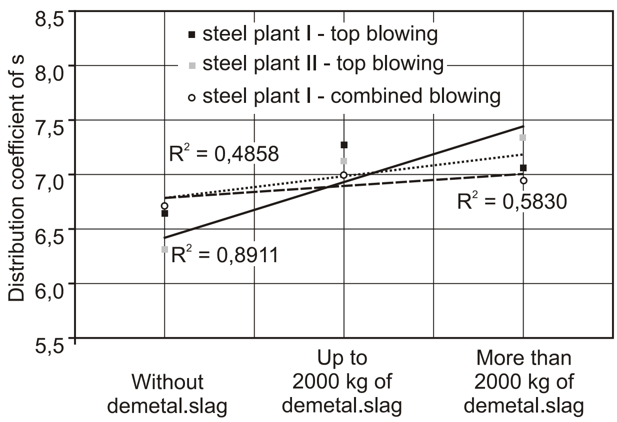

Figure 2. **Effect of demetallized slag recycling on desulphuration process in oxygen converter**
Slika 2. **Učinak recikliranja demetalizirane troske na proces otsumporavanja u kisikovom konvertoru**

Recycling of electric arc furnace slag [11]

Successful application of demetallized slag recycling into oxygen converter charge called new set of plant experiments with recycling of demetallized slag from electric arc furnace. The experiments were done in 60 t electric arc furnace with one slag regime when deoxidation, desulphuration, alloying and other processes were performed outside the furnace.

14 heats with addition of demetallized slag up to 800 kg were performed and sampled. Six heats were produced with decreased amount of charged lime, with substitution ratio lime - demetallized slag 1:2. Figure 3. shows that no

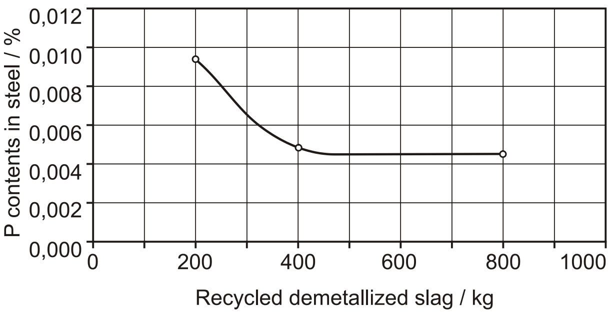

Figure 3. **Effect of demetallized slag recycling on dephosphoration process in electric arc furnace**
Slika 3. **Učinak recikliranja demetalizirane troske na proces odfosforizacije u elektrolučnoj peći**

negative influence of substitution was recorded. From the results of experiments followed:

1. Recycling of demetallized slag has no negative effects on parameters of smelting and refining in electric arc furnace, on composition of produced steel and its cleanness.
2. Recycling of demetallized slag can substitute a part of charged lime. Recommended substitution ratio lime - demetallized slag is 1:2.
3. For 60 t electric arc furnace recommended recycling rate is 800 to 1000 kg of demetallized slag per heat with corresponding decrease of charged lime 400 to 500 kg.

SLAG FROM LADLE FURNACE PROCESSES [12]

Because of composition and character of ladle furnace slag, no general instructions exist how to utilize it. Different kinds of steel require different ladle furnace methods for their production. Different kinds of slag are produced, most of them are dumped. This paragraph concerns a ladle furnace slag from steel tubes producing factory, where sortiment of produced steels is somewhat limited and ladle furnace methods are similar.

Table 1. **Chemical composition of LF slags, wt. %**
Tablica 1. **Kemijski sastav LF troske, tež. %**

	Fe	FeO	Fe_2O_3	SiO_2	CaO	MgO
LF 1	1,68	0,57	1,77	9,65	56,25	5,88
LF 2	1,67	1,29	0,96	9,31	56,34	13,04
	Al_2O_3	MnO	P_2O_5	S	Free lime	
LF 1	14,01	0,130	0,086	0,870	0,205	
LF 2	18,58	0,277	0,036	0,583	0,002	

Table 1. shows chemical composition of two samples of LF slags taken in the shop. Differences were found not only in chemical composition, but also in structural composition, colour and strength of the slags. Figure 4. represents structure of the ladle furnace slag with a few kinds of calcium silicates and RO-phase compounds.

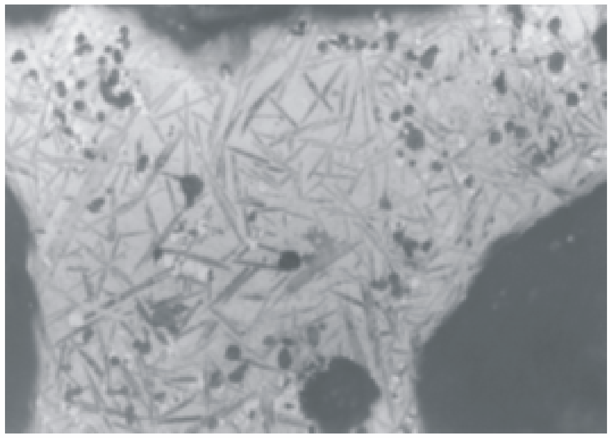

Figure 4. **Structure of ladle furnace slag LF2. Magnification 100×**
Slika 4. **Struktura troske metalurškog lonca LF2. Uvećano 100×**

LF slag, described in this paper, was proposed for utilization in cement producing factory. Because of high CaO, MgO, SiO_2 and Al_2O_3 contents the slag can substitute raw materials for cement production. The main problems for slag utilization were found in its transport properties. Some LF slag shows self - degradation features. Transport of very fine materials is encountered with many serious problems and is expensive. The research group from the Technical University proposed the method for compaction of fine sized LF slag.

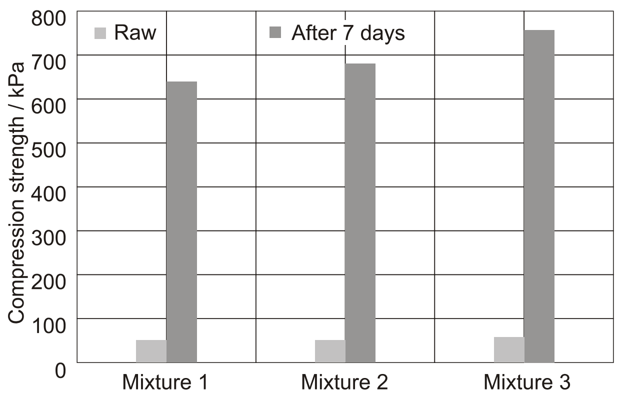

Figure 5. **Compression strength values of testing cylinders from LF slag**
Slika 5. **Vrijednosti tlačne čvrstoće ispitnog cilindra iz LF troske**

The first step of the treatment was crushing and grinding of LF slag pieces to the state when 85 % of slag grains had diameter less than 1 mm. Next three experimental mixtures were prepared.

Mixture 1: 3000 g LF slag + 150 ml H_2O;
Mixture 2: 3000 g LF slag + 150 ml H_2O + 30 g cement;
Mixture 3: 3000 g LF slag + 150 ml H_2O + 90 g cement.

The mixtures were prepared in laboratory mixer, next testing cylinders were pressed out (height and diameter of cylinder 50 mm) from each mixture. Compression strength of the cylinders was determined immediately after their preparation and after 168 hours - 7 days. Increase of the compression strength values after 7 days is in Figure 5. On the basis of experiments method of LF slag compaction was proposed. Technological scheme of LF slag compaction process is in Figure 6.

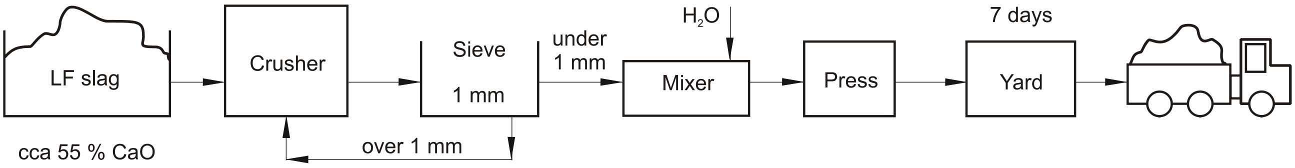

Figure 6. **Technological scheme of LF slag compaction process**
Slika 6. **Shema tehnološkog procesa sabijanja LF troske**

CONCLUSIONS

The paper has two parts. The first one consists of review of the most important processes used for treatment of blast furnace and steelmaking slags and of the most important ways of their utilization. Some problems encountered with use of blast furnace slag gravel and granulated blast furnace slags are mentioned. Similarly, methods of steelmaking slag ageing are described.

The second part of the paper deals with methods of steelmaking slag recycling. This part follows from experiments performed by the authors of the paper. Problems and benefits of the recycling of both oxygen converter and electric arc furnace slags are discussed. Proposals of recycling ways are also included. The paper finishes with proposal for utilization of one sort of ladle furnace slag.

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