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CORRELATION BETWEEN THE PROPERTIES OF OLD SLAGS AND THE RECYCLING SOLUTIONS

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ABSTRACT

The blast furnace and basic oxygen furnace route of steel making (from iron ores and coke to steel) or the so called integrated steel production generates simultaneously solid waste products. The slag is predominant, consisting of blast furnace (BF) slag and basic oxygen furnace (BOF) slag. The major share of this has been stored with no control near industrial area forming a metallurgical waste dump. For solving the problems of metallurgical residues and wastes stored in the old dump, the authority develops an appropriate environment policy for a proper management. The landfilled slag is exploited under supervision. The paper presents the sustainable recycling solutions applied in correlation with the properties of old slags. The performance of recycling solutions for each slag type is discussed according to the chemical composition and structure. Specific cooling conditions (as well as the chemical composition) of slag dumped under the action of variable weather conditions are analysed.

KEYWORDS: slag, dump, properties, recycling solutions

1. Introduction

The slag is the predominant co-product of the iron and steel making industry. An integrated steel mill plant generates different types of slag resulting from multiple sources/sectors. Iron and steelmaking slags (ferrous slags) are the most important. Additional slag types (e.g., de-sulphurisation slag of hot metal, ladle furnace or secondary steel making) are formed during diverse supplementary metallurgical processes (Figure 1).

The slags can be reutilized in various applications such as construction or agriculture. Also they come as valuable secondary raw for own sectors of integrated steel plants for internal recycling and for other users. EUROSLAG through its members (European steelworks and processing companies) has reported for 2010 a production of 45.3 million tons of ferrous slag (23.5 million tons of blast furnace slag and 21.8 million tons of steel slag). The steel slag produced in 2010 consisted of 48% BOF slag, 31% EAF slag (carbon steel), 13% secondary steel slag, 8% EAF slag (high alloy steel) and it was used in diverse application (Figure 2).

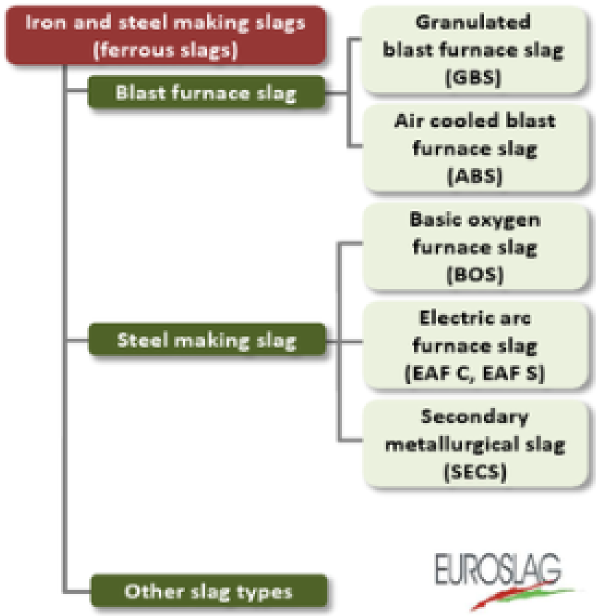

Fig. 1. *Slag families identified in Europe today* (Source: Euroslag.com)

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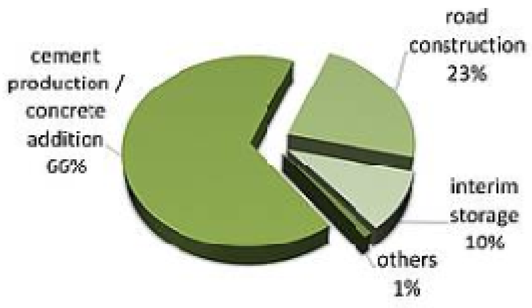
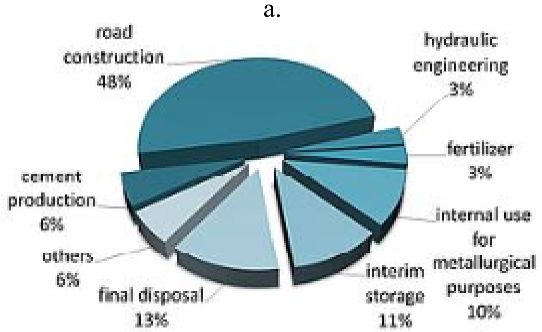


a.



b.

Fig. 2. *Use of ferrous metallurgical slag by EUROSLAG members in 2010 (Source: Euroslag.com): a. Blast furnace slag (Data from: A, B, FIN, F, D, I, L, PL, E, SK, S, NL, UK), b. Steel slag (Data from: A, B, DK, FIN, F, D, GR, I, L, PL, RO, E, SK, SLO, S, NL, UK)*

2. Research and discussions

2.1. Description of dump and of slags stored

The metallurgical plant of Galati was founded in 1961. It is located in Smârdan industrial park, occupying an area of 1.594 ha, at 3 km west of Galati. Here the steel is produced via the integrated route that uses a blast furnace to produce molten pig iron from iron ore, coke, and limestone. This pig iron is subsequently processed in a basic oxygen furnace to produce molten steel. Also for many years functioned within the plant an electric arc furnace sector where the steel was obtained exclusively by melting of steel scrap. In 1966, the plant started the production with one sintering plant, one blast furnace (1.700 cubic meters) and one steel melting shop [1]. On July 24, 2001, the government signed a privatization contract with LNM Holdings, the fourth largest world steel producer at the time [2]. The integrated steel mill plant has been acquired by ArcelorMitall Company. This was the largest steel producer of Romania, and the second largest in Central and Eastern Europe (Figure 3). The metallurgical plant has an estimated annual production capacity of 10 millions tons. After 1989 the production level was decreased to roughly half, from 8.4 to 4.5 ktones in 2003 [3]. Today it operates with a capacity of 5.5 million tons per year.

Fig. 3. *View of the integrated steel mill plant of Galati* (Wikipedia.org)

The blast furnace and basic oxygen furnace route of steel making (from iron ores and coke to steel) or the so called integrated steel production generates simultaneously solid waste products. Thus an average of about 400 kg of solid by-products is generated in the steel industry per ton of crude steel. The major share of this (70-80%) consists of blast furnace (BF) slag and basic oxygen furnace (BOF) slag [4].

The major solid wastes of the steel plant have been dumped. So since 1968, near the industrial area and Galati city, a metallurgical tailing dump has been formed from slag, used refractory materials, dusts, sludges and other mass waste (Figure 4).

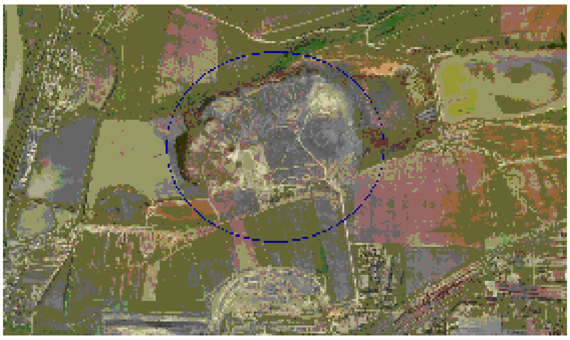


Fig. 4. *Image from satellite of landfill with location of the metallurgical wastes dump* (Google earth)

In 2002 the site had an area of 100 ha and heights ranging from 25 to 60 m [1]. This is currently called "slag dump" because the slag is the main metallurgical waste landfilled in cone-shaped heaps (Figure 5). Between 1968 and 2006 the slag dump has been landfilled with about 36.50 mil tons of blast furnace slag and approx. 14.50 mil.t of steel slag [5].

The wastes dumped are an ecological hazard. These are a permanent source of pollution to the environment and people's health.

***Fig. 5**. Huge piles of slag dump* [5]

The high cost of slag disposal, beside their negative impact on environment and the lack of natural aggregate resources, led to the reutilization of steel slag in various applications. According to the environmental Romanian national regulations (harmonized with the European legislation) was imposed a new approach for solving the problems of metallurgical residues and wastes: those stored in the old dump and the newly ones generated by the activity of the integrated steel mill plant. In 2009 the wastes storage in the historical dump was stopped completely. Also the authority develops an appropriate environment policy for a proper management, both the slags collected on dumps and the slags generated by ongoing production processes. Principally, there have been applied modern solutions to their minimizing at source. On the other hand, the wastes can be considered as a reservoir of valuable materials and consequently they must be valorised. So, by using the attractive solutions, there can be reduced and eventually eliminated the disposed wastes and thereby the minimizing of related environmental pollution. The saving of natural resources and energy is possible.

Considering the specific quantity produced for BF slag (ranged from 175–350 kg/t hot metal) and BOF slag (between 120 and 160 kg/t liquid steel) [6, 7], between 1968-2006 in the old dump of Galati have been deposited about 36.50 mil. tons of BF slag and approx. 14.50 mil. tons of steel slag [5]. Many efficient solutions to convert the metallurgical slag waste in a recyclable material have been applied. So, the slags from dump has lately been exploited and valorised. Despite the efforts there are still certain amounts of slags landfilled in old dump. Lately the Romanian authorities have intensified the efforts to eliminate from the historical dump the residual mill wastes located near Galati town. First, they strive to use slag in areas where they have demonstrated skills to use it. Secondly, they seek new solutions for its recycling. When adopting recycling, solutions must be correlated the properties of different types of ferrous slag exploited from dump with the technical requirements for the applying domain proposed.

2.2. Correlation between properties of ferrous slags and recycling solutions

The BF slag and BOF slag had some major differences in their chemical composition. The chemical composition and mineralogy determine the properties and the performance of recycling solutions for each slag type. In point of structure, all slags are unstable materials, subjected to changes under the action of variable weather conditions (temperature variations that determine the freezing and thawing in the presence of water, reactions between the slag and water/atmosphere, reactions caused by rain and changes in the pH of percolating water [8]). The cooling conditions (as well as the chemical composition) determine the formation of a crystalline or amorphous mineral structure, which furthermore influences durability, solubility and reactivity of the slags. Also the long-stay in the waste dump leads to mineral alterations by aging and disintegration. This involves the formation of secondary minerals through weathering of the primary minerals. At storage under weather conditions the transformations produced into slags are not complete.

The ***blast furnace slag*** dumped is a homogeneous material. On average, the blast furnace slag contains about 0.5–0.8 % FeO, 35–42% CaO, 35–40% SiO_2, 8–9% MgO, 8–15% Al_2O_3, 0.3–1.0% MnO and 0.7–1.5% S in weight. The slag basicity CaO/SiO_2 is in the range of 0.95–1.25 [9, 10]. The results of analytical quantitative determinations showed the main oxides existent in the ferrous slags from Galati metallurgical plant (Table 1) [11].

The mineralogy and physical properties of this slag are influenced by itschemical composition and cooling conditions. The literature shows that the most common minerals found in the air-cooled blast furnace slag are akermanite, gehlenite, wollastonite, dicalcium silicate, merwinite, anorthite, monticellite [12]. The liquid slags were discharged to waste dump by ladles and naturally cooled into ambient air with temperature variable depending on the season. So, it has been provided a slow cooling by air contact from around 1500 °C (the tapping temperature of slag from blast furnace) and it was formed a crystalline structured rock-like mass. The degree of crystallization depends primarily on the mineralogical structure of the basic constituents of slag. In slow cooling, BF slags precipitate into crystallized silicate phases (for example, melilite and merwinite). The main component of basic slags is dicalcium silicate. This compound has the property that at a slow cooling it goes through several states. Its structural changes, accompanied by volume expansion of approximately 12vol-%, can convert the slag into a powdery material. For the slag dumped the alteration of minerals can occur due to weathering processes in nature. The minerals react with moisture, CO_2, etc. during storage and to some degree they undergo phase transformations [13]. This is the so called mineral aging process, when a primary mineral undergoes transformation and a secondary mineral is formed. In slow cooled slag the only crystalline compound which has cementitious properties is β-$2CaO{\cdot}SiO_2$. Due to the low iron content, the BF slag is not considered as valuable iron-rich waste justified to be recovered in steel mill plant. After excavation this is sorted, crushed and valorised as aggregate, ballast and lightweight building material, not as a cementing component.

Table 1. *Composition of metallurgical slag from metallurgical plant Galati*

Type of slag	Chemical composition, [%]								
	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	Other	S
BF slag	41	7-8	36	7-9	0.8	0.5-0.8	0.2-1	~1.3 (P)	0.8
Steel slag	42-44	5-7	30-35	2.5-3.7	15-20	2.5-5	3-6	~0.5 (Cr and V)	-

The ***steel making slags*** stored in dump are BOF slags and EAF slags. Their chemical properties are variable. So is more difficult to use the steel slags compared to the BF slag. On average, the BOF slag in literature has Fe 2–8%, CaO 40–60%, MgO 3–10%, MnO 1–8%. The slag basicity from BOF slag is in the range of 3.5. The major phases present in LD slag are dicalcium ferrite, calcium alluminate and wüstite, but it contains also some reactive mineral phases, such as $2CaO{\cdot}SiO_2$, $3CaO{\cdot}SiO_2$, free CaO and MgO [14, 15]. These are observed in microstructures of slags samples presented in Figure 6.

There are steel slags collected from two areas of the dump.

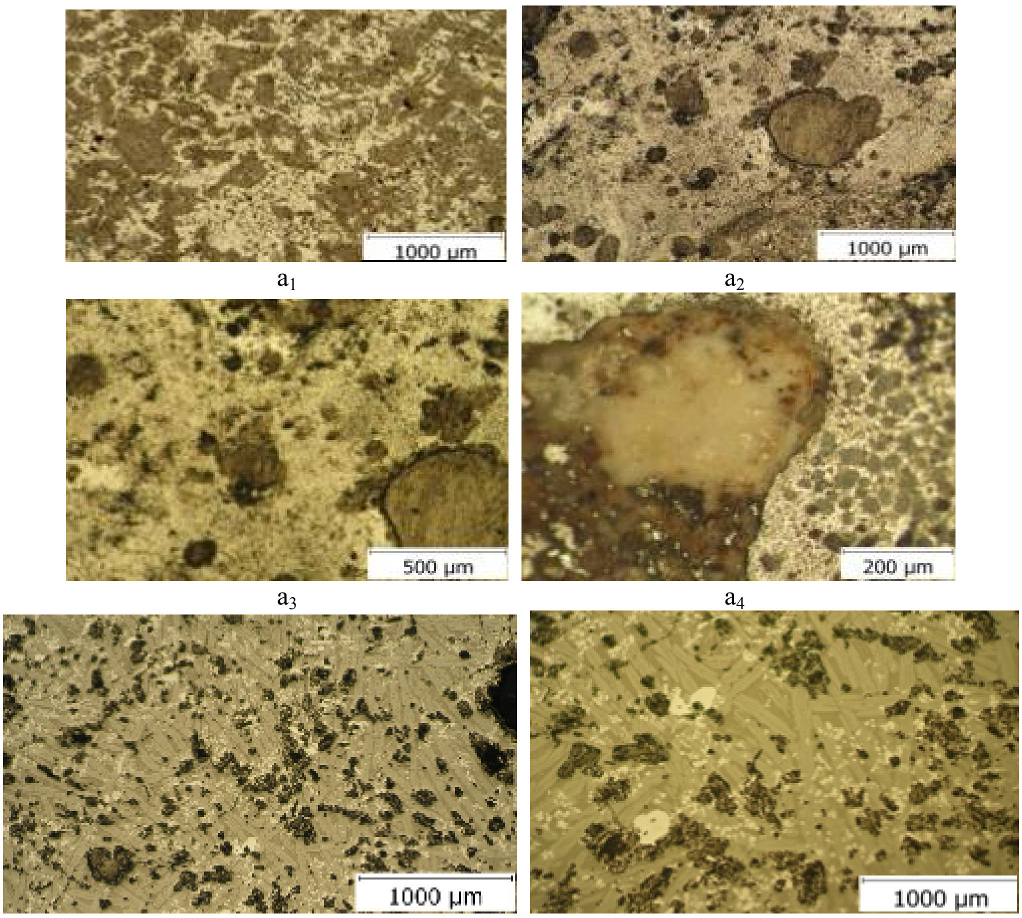


Fig. 6. *Microstructures of samples of steel slag collected from dump*

The presence of metallic phase can be observed. This is distributed into matrix of slag as white and bright globular formations. A non-uniform structure with very different distribution of metallic phase was observed. In some areas the metallic phases are absent, and other areas are rich in such phases.

The metallic phase appears as bright white formations, predominantly globular. These are dispersed in a matrix of iron silicate with variable proportion of iron oxides (wustite and magnetite). Some vitreous phase was observed. Free CaO (and MgO) has been found in the slags from the integrated steel plant of Galati (Table 1) [11]. Because of their lime contents (and periclase) they expand in reaction with water. After this expansion they can be stabilized by "natural ageing" for long periods outdoors in natural rainfall [16]. The slow cooling under natural condition of humidity and the longer stationary period in the dump can ensure the conditions required for minerals crystallizing and chemical stabilization of this slag. 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) [11].

Also these steel slags (in comparison to BF slags) have higher iron contents than oxides or than fine metallic particles.

The removal of metallic iron from the slag by magnetic separation is necessary. Due to the high content of iron oxides, the steelmaking slags must be exploited for an efficient recovering of their valuable iron units. Magnetic products may be utilized as a component for sintering mixture.

2.3. Valorisation solutions of old slags

The impressive slag dump near Galati can be considerably reduced by introducing into the economic circuit the mineral aggregates obtained by processing metallurgical slag in accordance with legal requirements.

The metallurgical slag as aggregates is valorised in various applications in the construction industry. Their performance characteristics have proved effective in their use in Romania since 2002.

The steel slag is exploited from slag dump by mechanical operations: excavation, transport, crushing, milling, magnetic separation, and screening (Figure 7).

Fig. 7. *Plant for exploitation of old slag* [16]

Several different types of materials with variable iron content and different grain size are obtained: larger pieces of the steel scrap; diverse non-magnetic fines or coarse non-magnetic fractions. Also, the non-magnetic fractions are sorted by classes, more or less rich in iron.

The high iron fractions sorted from steel slag are valuable for internal recycling into sintering process. The nonferrous fractions are transferred into a special zone. Here the slag is treated for ageing about six months by an amount of water that is sprayed onto its surface. In this way are reduced the expansive oxide contents.

The slag aggregates called *Lidonit* are obtained from steel slag excavated from the slag dump of Galati.

From the technological point of view, the obtaining of this product is similar to the classical method for producing natural aggregates exploited from rock quarry [17].

Only a supplementary pre-treatment for removal of metallic rich iron fractions from the slag by magnetic separation is necessary.

After crushing, sieving and removal of magnetic matter, they achieve granularity appropriate to different applications. Another product from slag named *Benolite* is currently undergoing certification for use [18].

The slag from blast furnace is processed through a screening and crushing plant and is processed into many sizes for use primarily as a construction aggregate.

3. Conclusions

The metallurgical slags landfilled in the dump located near Galati are a permanent source of pollution of the environment and people's health.

The EU Directives and national legislations demand their elimination. Also the remediation and restoration of areas contaminated are imposed. The recycling solutions can be applied. For each type of slag (BF slag and steel slag) the solution that must be applied are different.

The solution is also different as fo the new slag generated by the activity of integrated steel mill plant. The chemical composition, cooling condition, action of variable weather conditions lead to some structure transformation in the slag dumped. Several different types of structures and fractions of slag with variable iron content and different grain size are observed. The slags processed in special flow are used primarily as construction aggregates.

The high iron fractions are recycled in the steel plant of Galati, into sintering process.

References

[1]. *** - *Local Agenda 21 – Local plan for sustainable development of Galati municipality*, 2002.

[2]. A. Sznajder - *Effects of EU Accession on the Politics of Privatization*, The Steel Sector in Comparative Perspective, http://blog.richmond.edu/asznajder/files/2008/02/sznajder_erbe_des_beitritts.pdf.

[3]. R. Berger - *Romanian Steel Industry: Forging ahead*, Romanian Business Digest, 2004.

[4]. *** - *Management of Steel Plant Solid Wastes*, http://www.tifac.org.in/index.php?option=com_content&id=736&Itemid=205.

[5]. M. Luca, R. P. Balan - *Monitoring the exploitation of the industrial waste dump*, Buletinul Institut Pol. din Iasi, Tomul LIV (LVIII), Fasc. 2., Hidrotehnica, 2008, p. 25-36.

[6]. *** - *Eurofer,* Review blast furnace slag processing, 2007, p. 5.

[7]. M. H. Joulazadeh, F. Joulazadeh - *Slag; Value Added Steel Industry Byproducts*, Archives of Metallurgy and Materials, vol. 55, Issue 4, 2010, p. 1137-1145.

[8]. Y. Sueoka, M. Sakakibara - *Primary Phases and Natural Weathering of Smelting Slag at an Abandoned Mine Site in Southwest Japan*, Minerals, 2013, 3, p. 412-426.

[9]. M. Reuter, Y. Xiao, U. Boin - *Recycling and environmental issues of metallurgical slags and salt fluxes*, VII International Conference on Molten Slags Fluxes and Salts, The South African Institute of Mining and Metallurgy, 2004.

[10]. J. Brito, N. Saikla - *Recycled Aggregate in Concrete*, Use of industrial, Construction and Demolition Waste, Chapter 2, Industrial Waste Aggregates, 2013, www.springer.com.

[11]. M. Cioroi, L. Nistor (Cristea) - *Recycling Possibilities of Metallurgical Slag*, The Annals of "Dunarea de Jos" University of Galati, Fascicle IX, Metallurgy and Materials Science, no. 1, 2007, p.78-82.

[12]. D. W. Lewis - *Properties and Uses of Iron and Steel Slags*, Symposium on Slag National Institute for Transport and Road Research South Africa, February, 1992, http://www.nationalslag.org.

[13]. S. Diener - *Mineral phases of steel industry slags used in a landfill cover construction*, Master thesis, Technische Universität Dresden, 2006.

[14]. T. A. Branca, V. Colla - *Possible Uses of Steelmaking Slag in Agriculture: An Overview*, www.intechopen.com.

[15]. F. Engström - *Mineralogical Influence of Different Cooling Conditions on Leaching Behaviour of Steelmaking Slags*, Licentiate thesis, Luleå University of Technology, Department of Chemical Engineering and Geosciences, Division of Process Metallurgy, 2009.

[16]. *** - *Lidonit. Agregate din zgura de otelarie*, http://www.dsu.ro/ro/lidonit.php.

[17]. L. Cristea - *Utilizarea agregatelor Lidonit la construcțiile de drumuri*, Revista Construcțiilor decembrie 2012, p. 38-39, http://www.revistaconstructiilor.eu.

[18]. L. Cristea, D. Iofcea, M. Badiu - *Atestarea conformitatii agregatelor „Benolite" pentru aplicarea marcajului CE*, Revista Constructiilor, nr. 83, iulie 2012, p. 36.