BEHAVIOUR OF LADLE SLAG PRIMARY AND SECONDARY MINERALS IN SLAG HEAP CONSIDERING UTILISATION

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Abstract: Secondary steelmaking slags contain numerous types of minerals such as larnite and various Ca-aluminates. Fresh ladle slags are unstable in the atmosphere disintegrating into fine white dust. The modification change of larnite (C_2S) is the main cause of this phenomenon. The freshly formed white slag powder is unprotected against wind erosion. When water is sprinkled on it, however, a solid crust is formed instantly. According to the results, this hard layer contains calcium aluminate hydrate causing quick bonding and reducing the threat of wind erosion significantly. The major composing minerals of slags belong to two groups: the gehlenite–akermanite series belonging to sorosilicates and the larnite–bredigite series that belong to nesosilicates. In very small quantities these slags also contain various heavy metals. The most characteristic among them is barium that is mostly precipitated as non-soluble barite in the course of the disintegration of the slag therefore it presence no environmental risk. The chemical composition of slags determines their possible utilization which is also discussed in the paper.

Keywords: minimill, ladle furnace, deoxidisation, oldhamite, skarn minerals, gehlenite, tobermorite, larnite, OAM Ltd.

1. INTRODUCTION

The first step of steelmaking is the so called primary steel metallurgy. In this way the charged material is oxidized. In the course of this stage the uptake of oxidable nondesirable elements such as Si, Mn, P into the slag phase in the forms of SiO_2, MnO, P_2O_5 takes place. At the same time, the initial S content of the steel decreases significantly (max. 50%) while it is absorbed in the slag. The most widespread technology of primary steelmaking is very similar at both the integrated steelworks and minimills, however, some differences may occur. At the integrated steelworks mainly Basic Oxygen Furnaces (BOF) are in operation that consume the blast furnace produced hot metal (Simon et al., 1980). Therefore in the BOF area the main charging material is hot metal (75%) with well known quality and the rest is carefully separated scrap (25%) containing nondesirable elements in relatively low concentration. In this case, the application of the „catch carbon heat" technology is possible, in which the heat is under oxygen blasting until the carbon content decreases to the desirable level and then the steal is tapped. Steel produced in this way contains relatively low concentration of dissolved oxygen resulting in the lower consumption of deoxidants. Nowadays this method is advancing worldwide. Most BOF melt shops use „building up heat" technology including the total oxidisation of carbon from the batch. In this way the bath becomes almost completely void of C, Si, P, Mn. It is carburised during tapping and the steel is treated in the ladle. Application of this technology is often reasonable because steelmakers can produce relatively clean raw steel from contaminated raw material for secondary steelmaking facilities.

Numerous phase changes and their environmental effects have been studied at Ózd

Steelworks Ltd. (NE Hungary). Vast amount of data and publications are available for understanding and analysing of traditional steelmaking at Ózd with 150 years of history (Berend, 1980; Óvári, 1985; Remport, 1995; Vass, 1996; Vorsatz, 2000; Sziklavári, 2009). Processes and environmental effects of minimill steelmaking at Ózd with a history of only two decades have also been studied and analysed. The present paper gives an outline of some selected results of these studies.

Minimills operate with 100% scrap ratio. The Ultra High Power (UHP) Electric Arc Furnace (EAF) is the soul of this type of mill (Szőke, 1990). The most widespread technology applied in minimills is the "building up heat" technology mentioned above. The scrap charge is melted down by an electric arc and oxyfuel jetburners as is the case at Ózd Steelworks Ltd. (OAM). By the end of the process the batch becomes oversaturated in oxygen. If gases released as the melt cools formed vesicles in the solidifying steel the quality of the product would be deteriorated. The presence of inclusions in the steel and its high sulphur content could also cause problems. In such cases, the product fails the quality requirements of steel standards.

Such quality problems can be avoided if secondary refining is applied (Póczos, 2000). Secondary steelmaking technologies can be divided into two groups substantially: atmospheric and vacuum technologies. In order to meet the requirements various ladle metallurgical technologies are applied in minimills (for example: vacuum technologies: VOD, ASEA-SKF, etc.) (Szőke, 1990).

The most advanced and fundamental technologies, however, use no vacuum and the batch is kept under atmospheric conditions. One of these is the atmospheric gas purging (AP) where inert gas (N_2, Ar) flows into the ladle at the bottom via a purging plug. The gas input steers the steel melt and promotes its homogenisation. The standard technology consists of two technological steps. The first step is precipitation deoxidation while the steel is under tapping. The second step is diffusion deoxidation carried out in a ladle furnace where the steel obtains its final composition and inclusions float into the slag and where they are absorbed (Simon et al., 1980).

Slags forming here can be regarded as artificial rocks resembling the characteristics of natural skarn zones that can be found and observer all over the volcanic regions of the Carpathian Basin (Kónya & Zajzon, 2015). Utilization of such slags is yet to be solved worldwide as they present serious environmental risk in numerous places where this by-product is disposed as waste material.

Elimination of the environmental risk presented by industrial waste material, by-products, slags among them accumulated in the industrial districts of the former socialist countries in Central Europe accumulated over a long period of time require major measures. The area of OAM Ltd studied in the present paper is one of the three largest industrial areas in Hungary with such problems.

For effective management, utilization and recycling of ladle slags in the future their physical and chemical parameters have to be known in detail. The present paper aims to contribute to the advancement of knowledge and information regarding ladle slag.

2. MATERIALS AND METHODS

Samples were taken from the three most typical slag types including disintegrated (Fig. 1), dissociated white lumpy (Fig. 2) and brownish grey lumpy ladle furnace (LF) (Fig. 3) slags. For thermal analysis another sample was taken from the bonded LF slag (Fig. 4). Chemical and thermal analyses were carried out at the Geochemical Laboratory of the University of Debrecen. Samples were crushed and pulverized below 0.63 µm in diameter prior to the analyses. Bulk analysis was carried out using a RIGAKU GEIGERFLEX SYSTEM 3063P type WDXRF spectrometer except for Mg and Na the quantity of which was determined using a ZEISS AS1 type FAAS Spectrometer. H_2O content was measured by loss of ignition at 1000°C (LOI1000). Trace elements were determined using a Spectro flame ICP-OES spectrometer (Papp, 2002) in the laboratories of Analab Ltd., Debrecen. Calibration was carried out by standard stock solutions produced by Merck. Thermal analysis for determining secondary minerals was carried out using a MOM Derivatograph (Tamás, 1970) with PC evaluation. For this analysis samples were taken separately from the weathered slags solidified years ago with advanced hydration and carbonization (Fig. 4). Thin section analyses were also made at the Department of Mineralogy and Geology, University of Debrecen using a Nikon Microphot SA type polarization microscope with a digital camera. Thin sections were 30 µm thick.

X-ray phase analysis was carried out at the XRD Laboratory of the Geological and Geophysical Institute of Hungary using a Philips PW1710 type diffractometer with an XDB Power Diffraction Phase Analytical System 2.7 software controlled measuring and evaluation system, and with the use of PDF database. SEM and microprobe analyses were performed in the SEM Laboratory of the Institute of Material Science, University of Miskolc using a ZEISS EVOMA 10 type scanning electron-microscope with an AMETEK type microprobe unit.

Figure 1. Disintegrated secondary slag in the slag heap of OAM Ltd.
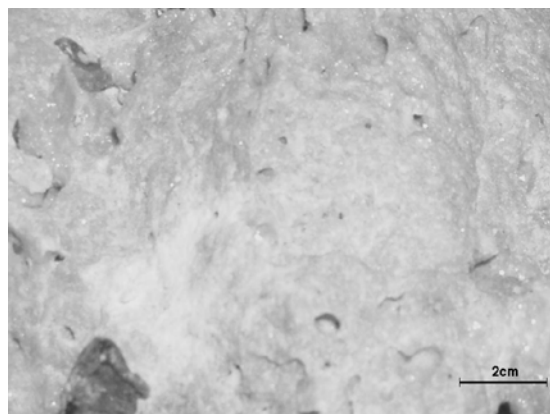

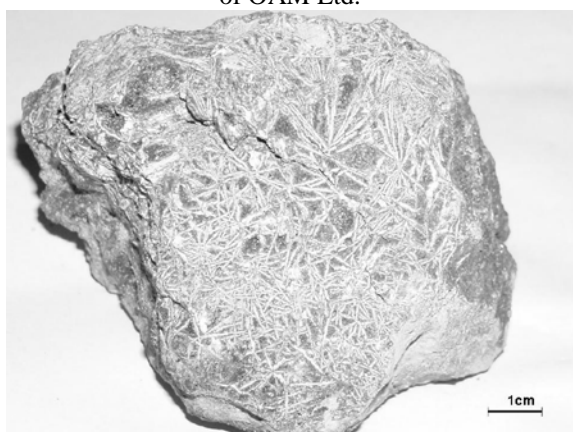Figure 2. White lumpy LF slag in the slag heap of OAM Ltd.

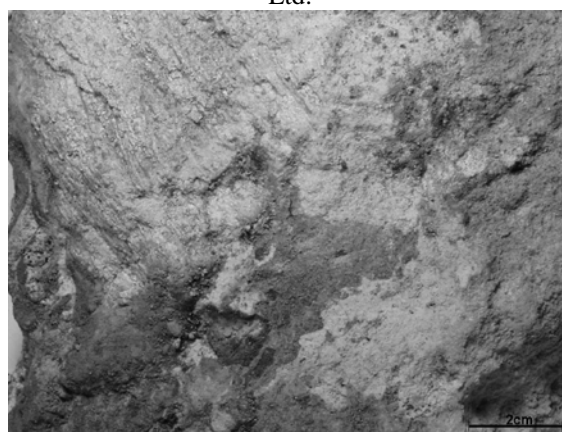Figure 3. Brownish grey LF slag from the slag heap of OAM Ltd.

Figure 4. Hydrated, bonded LF slag in the slag heap of OAM Ltd.

3 RESULTS AND DISCUSSION

3.1. Mineralogical effects of secondary metallurgy

At the end of the minimill process the ladle treatment of the steel is started while the EAF is being tapped. In this way flux additives and deoxidant agents are added to the steel flow. Deoxidants include ferroalloys (FeMn, FeSi, FeSiMn, etc.) and aluminium while flux additives include lime, alumina, alu-slag, fluorite and coke powder as carburiser agent (Póczos, 2000). Ferroalloys and aluminium react with the active dissolved oxygen therefore the initial oxygen content decreases (20-30 ppm). This technological step is called precipitation deoxidation, where oxygen forms various oxides and silicates. The forming particles in the bath are different minerals like fayalite (Fe_2SiO_4) – knebelite (Mn_2SiO_4) series, cristobalite (SiO_2), corundum (Al_2O_3), hercynite ($FeAl_2O_4$), etc. Since their density and grain size are different the velocity at which they float up into the slag is also different. This can be calculated based on Stokes' law (Simon et al., 1980).

Particles unable to float into the slag form inclusions in the steel. Residual minerals such as within the inclusions such as corundum and mayenite ($Ca_{12}Al_{14}O_{33}$) may cause the clogging of the well block making casting disturbed and problematic. Thermal expansion of the inclusions is different from that of the steal causing structural stress and eventually deteriorating the steel product. To absorb the products of deoxidation or transform them into non-harmful inclusions lime flux is added to the melt. The resulted basic slag and the reductive environment enable effective desulphurisation (Simon et al., 1980) as a result of which the sulphur content of the steel melt is precipitated as metal sulphides like FeS (troilite), MnS (alabandite), $(Ca,Mg)S$ (oldhamite) and $(Mg,Fe^{2+},Mn)S$ (niningerite) that in the end float up into the slag. Gas purging via the purging plug in the bottom of the ladle generates circulation in the melt towards to the slag and down to the bottom of the ladle. In this way – while the ladle is transported to the ladle furnace stand – inclusions and other reaction products float up, and the dissolved gas content (CO, N_2, H_2) decreases as well.

Three graphite electrodes are set in the melt with which the bath is heated until its temperature

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reaches that required for casting. At the same time the circulation of the melt remains continuous and the oxygen content decreases further. The latter process is diffusion deoxidation, because the equilibrium of FeO and MnO concentrations in the metal /slag phase is modified. That means lower FeO, MnO concentrations are kept in the slag by the addition of deoxidation agents such as Al, FeSi powder, CaSi and coke powder. The reduced metal flows back into the steel bath. As a result the dissolved oxygen content of the steel is reduced below 100 ppm providing appropriate conditions for desulphurisation of the steel.

Processes during desulphurisation are quite similar. Directly around the electrodes the temperature is as high as 6000-7000°C that enables the possible formation of carbides (CaC_2, Mg_4C_3, SiC, Al_4C_3, etc.), however, hypothetically different fullerens, metallokarboeders may also form. The added lime flux forms clinker like minerals (Taylor, 1997) with the products of deoxidising that cannot be disintegrated, e.g. corundum and a few silicates. Such minerals are the following: calcium-aluminates (e.g. dicalcium aluminate /$2CaO \cdot Al_2O_3$ (C_2A)/, tricalcium aluminate /$3CaO \cdot Al_2O_3$ (C_3A)/, and mayenite ($Ca_{12}Al_{14}O_{33}$), silicates together with Ca_2SiO_4 (larnite), Ca_3SiO_5 (hatrurite), gehlenite-akermanite ($Ca_2Al[AlSiO_7]$ – $Ca_2Mg[Si_2O_7]$), etc. (Drissen, 2000; Bradškaja et al., 2004). The sulphur content forms MnS – alabandite, CaS – oldhamite, MgS – niningerite, (Fe^{2+}, Mg, Ca)S – keilite series. Precipitated calcium-aluminate grains affect sulphides like mineralisators, because floating aluminate inclusions can adsorb sulphur on their grain surface as oldhamite layers (Seilerová et al., 2004).

3.2 Chemical composition of secondary slags

Considering the major element composition of the slags (Table 1) some differences in the SiO_2 and CaO content can be traced in the physical condition of these slags as well. They are match to our theory. The dissociated slag contains high amount of lime and magnesia and some amount of different kinds of calcium aluminates. As a result, these slags are basic due to the excess amount of lime. Apart from the

transformation of larnite, the hydration and carbonatisation of these free oxides are very important reactions that can contribute to the dissociation of the slags. XRD analyses prove the above because the secondary formations as spurrite ($Ca_2SiO_4 \cdot xCaCO_3$) and calcite ($CaCO_3$) are found. The brownish grey lumpy slag contains relatively high ratio of SiO_2 (Table 1).

The definition of basicity is given as below:

$$B_3 = \frac{CaO\% + MgO\%}{SiO_2\% + Al_2O_3\%} \qquad (1)$$

where SiO_2 and Al_2O_3 are the acidic components and B_3 – basicity is interpreted as $B_3<1$ acid, $B_3=1$ intermediate, $B_3>1$ basic (ideal) (Koleszár & Papp, 2010).

The brownish grey slag has a basicity of $B_3=0.99$, meaning that it is intermediate or slightly acid. This is an inefficient and harmful melt, because it cannot absorb any sulphur, but corrodes the refractory lining of the ladle (Nicolae et al., 2011). Furthermore its freezing temperature is relatively low with ~1400°C (Fig. 5). Therefore its viscosity is very low at the operation temperature and is similar to that of the blast furnace slag. The most effective slag is the white lumpy one with $B_3=1.85$. Due to its relatively high ratio of alumina content its solidus is around 1455°C. The dissociated one is moderately effective with $B_3=1.46$. So they are, efficient desulphuriser slags. Freezing temperature of the dissociated slag is around 1545°C which is higher than that of the steel by some 25°C.

Slags composed mostly of gehlenite are disadvantageous since the temperature of their solidification is at 1593°C. Such slag solidifies on the surface of the steel in the ladle early at the beginning of steel casting. Level of the steel in the ladle decreases below the slag crust solidified at the mouth of the ladle. Steel surface without slag cover can take oxygen and nitrogen from the air that may deteriorate the quality of the steel product when the nitrogen is present in the steel in more than 140 ppm. Slags studied in the present paper are not problematic in this respect since their freezing point (as shown in Fig. 5) varies between 1400 and 1545°C (below the freezing temperature of steel).

Table 1. Major element composition of ladle slags (m/m%)

Analysed samples: 1. white dissociated slag, 2. white lumpy slag, 3. brownish grey acid slag

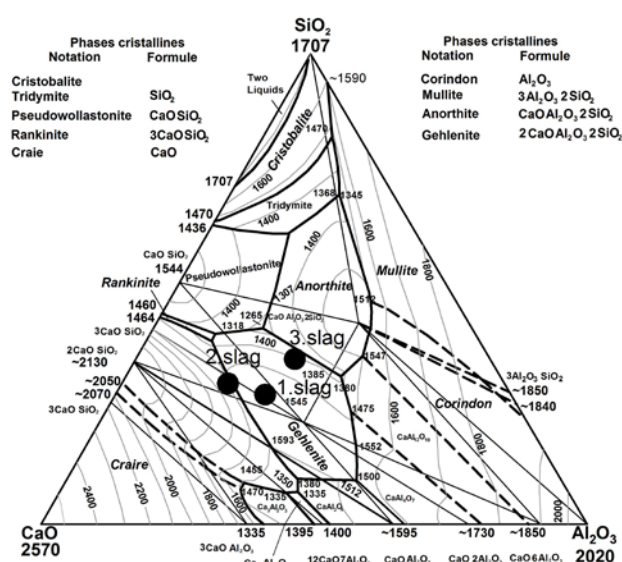|	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	S	H_2O	other
method	XRF	XRF	XRF	XRF	AAS	AAS	XRF	AAS	XRF	XRF	XRF	gravimetry	
1.	20.6	0.05	17.6	1.30	0.32	7.27	48.3	0.03	0.35	0.15	0.67	0.27	3.09
2.	16.1	0.03	17.0	0.67	0.00	5.83	55.1	0.06	0.35	0.14	1.89	0.64	2.19
3.	25.7	0.02	21.0	1.11	1.19	8.31	38.0	0.10	0.34	0.09	0.09	0.36	3.78

Figure 5. Position of ladle slags in the CaO – Al$_2$O$_3$ – SiO$_2$ ternary diagram. (Legend: 1. white dissociated slag, 2. white lumpy slag, 3. brownish grey acid slag) (after www.ulab.eu)

Solidification at 1545 °C causes no problems in theory, however, solidification of the slag sometimes at this late stage of casting makes it strongly viscous therefore it is difficult to pour it out of the ladle.

In extreme cases, slags remaining in the ladle may increase the sulphur content of the next charge by 0.01 %, however, it may also help the equal solution of the slag forming lime. This is the reason why easy flowing slag forms hardly when the melt is tapped into freshly lined ladle.

Apart from composition the temperature of slags during operation also influences significantly the effectiveness of desulphurization. According to our experience, no significant desulphurization takes place in the steel under 1600°C. Optimum temperature for desulphurization is 1620°C. No matter how good is the composition of the steel the demanded desulphurization fails if temperature is not right. Third important factor of optimal desulphurization is small FeO content of the slag (Bulko et al., 2009). This condition is generally met in the case of the studied slags (Table 1).

According to the trends, the white lumpy slag has the greatest sulphur content, because this is the most basic slag. Considering the composition of the dissociated slag it seems like it would be the mixture of the most basic white lumpy and the more acid brownish grey slags. The stability of the lumpy slags is improved by their MnO and FeO content.

Considering the trace element composition of the studied slags, several heavy metals may occur in them, however, their quantity is very low (Table 2). Only Ba and Sr may become enriched somewhat.

Barium presents some environmental risk, however, only in certain circumstances. According to our analyses, barium precipitates with sulphate containing leachate in a non-soluble sulphate form as barite therefore it presents no environmental risk at OAM Ltd. Due to the reductive character of the slags in the technology applied at OAM chromium is present in the form of Cr^{3+}. Considering the reductive conditions, there is no chance for the presence of hexavalent chromium (Cr^{6+}). Trivalent chromium is built into the structure of gehlenite, because it can substitute aluminium in the crystal lattice. The rest of the trace elements like Zn, B, Cu, Se, etc. are essential trace element for plants.

3.3 Mineralization of secondary slags

The white and the brownish grey slags were studied under a reflective optical microscope as well. The samples were polished in a wet medium resulting in the water etching of the investigated surface. Water etching is especially useful in the case of white lumpy slags (Fig. 6) because inhomogeneities of the polished surface were exposed. This method resulted in no notable features. Water etching helps to predict the watertightness and stability of the slags. Figure 6 shows columnar (rhombic) crystal groups that could have been tricalcium silicate crystals originally but they disintegrated into two phases during slow cooling. One of them is a lime rich phase (blue parts in Fig. 6) while the other is abundant in larnite-bredigite (light brown parts in Fig. 6). Scattered white patches are various aluminates, e.g. mayenite.

Table 2. Trace element composition of ladle slag types (in ppm)

Slags / g/t	As	Ba	B	Cd	Co	Cr	Cu	Mo	Ni	Se	Sn
Dissociated	<1	883	116	<0.25	<0.25	38.6	66.0	<0.25	<0.5	2.0	1.0
White lumpy	3.4	434	53.9	<0.25	<0.25	5.3	29.8	<0.25	<0.5	1.3	<0.5
Brownish grey lumpy	<1	922	169	<0.25	<0.25	81.9	20.0	<0.25	<0.5	3.2	<0.5
Detection limit	1	1	2.5	0.25	0.25	5	1.5	0.25	0.5	0.5	0.5

Figure 6 also reveals the effect of slow cooling, the dissociation of tricalcium silicate, in other words hatrurite (Ca_3SiO_5). When Al replaces Si in the structure of the silicate its dissociation slows down or terminates completely. In this case tricalcium silicate remains stable at room temperatures as well (Taylor, 1997).

In Figure 7 the slightly acid brownish grey slag can be seen. As it is saturated in silica the major mineral phases are rich in group silicates including akermanite–gehlenite series (dark phases). In the minor phases nesosilicate minerals also occur (light phases) including the larnite–bredigite series. The dissolution of the above mentioned major phases in each other is limited at around 1550°C therefore they tend to form eutecticum. Such eutectic texture is shown in figure 7 where white lenses of the minerals of the larnite–bredigite series appear in the dark matrix.
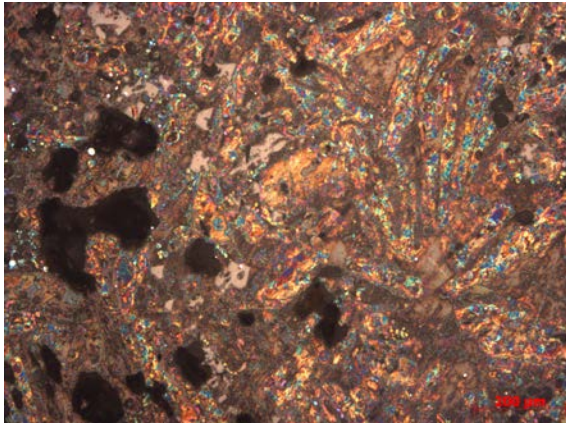

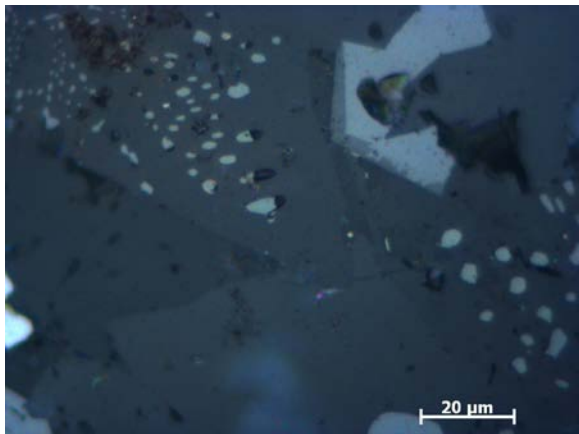Figure 6. Thin section of a white lumpy slag sample under a reflective optical microscope

Figure 7. Eutectic texture of a brownish grey slag sample under a reflective optical microscope

Mineral phases were identified based on XRD measurements that supported the presence of the assumed minerals in the slags. Periclase (MgO) occurred as separate phases in the dissociated slags in small quantities (Fig. 8). Sulphides form pyrosols

dispersed in the slag as colloid scale particles that cannot be detected using the XRD method. Since they smell like rotten egg when contacting with water their presence in the dissociated and the white lumpy slags can be observed.

Based on the analyses, the vast majority of the total mineral phases belong to two groups (Table 3): the mellite group (gehlenite–akermanite series) and the larnite–bredigite group. Minerals of the two groups are common in all of the slag types, however, their ratio can be different (Figs. 8–10). The third major group that gives only a few percent of the minerals is the calcium aluminate group.
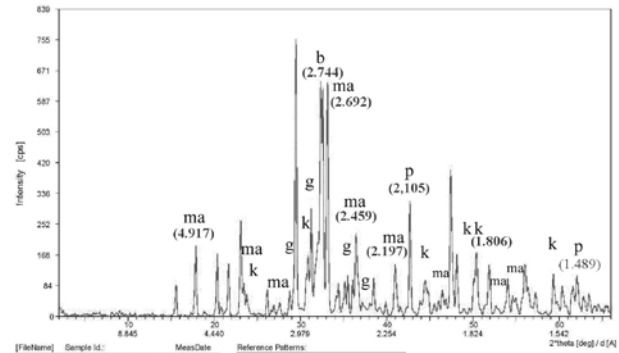

Figure 8. XRD diffractogram of the dissociated LF slag (legend: b: bredigite; g: gehlenite; k: kutnahorit; ma: mayenite; p: periclase)
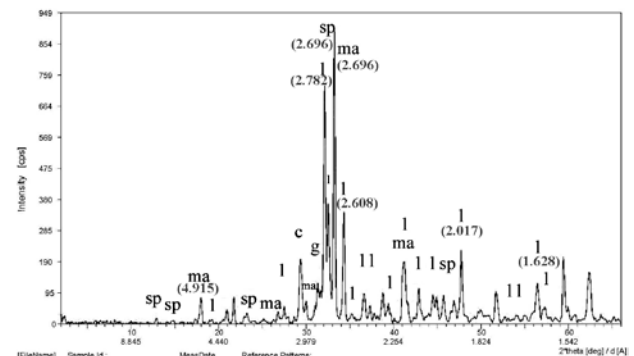

Figure 9. XRD diffractogram of the white lumpy LF slag (legend: c: calcite; g: gehlenite; l: larnite; ma: mayenite; sp: spurrite)
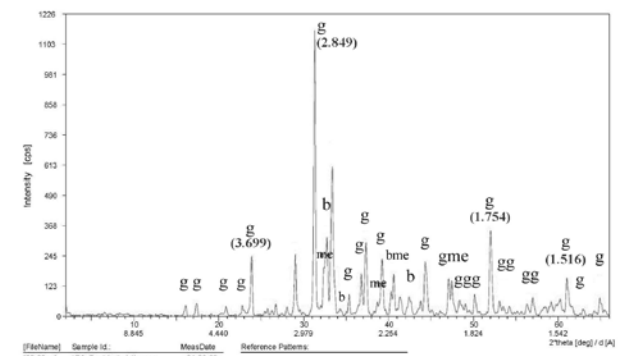

Figure 10: XRD diffractogram of the white lumpy LF slag (legend: b: bredigite; g: gehlenite; l: larnite; ma: mayenite; me: merwinite)

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Mayenite ($Ca_{12}Al_{14}O_{33}$) is the most important mineral among the calcium aluminate group occurring mostly in the white, dissociated, basic, secondary slags. Several accessory minerals may occur in the slags, however, most of them are present in very small quantities therefore their detection is difficult. Their structure presents another problem. They form colloid scale crystal rudiments that are at the transition between crystalline and non-crystalline states. We have detected some accessory phases using SEM including alabandite, perovskite, Cr_2O_3. Even pyroxenes were identified in thin section. In our opinion these could be enriched by some kind of selective dissolution (using for example HF). This was not necessary in our case since the most important characteristics of the three slag types depend on the ratio of the mellite and larnite minerals and that of the calcium aluminates. The ratio of the residual, non-dissociated material in the total mass is about 5-10%. In our opinion SEM analyses prove that the free magnesium oxide content of the slags can promote their dissociation (Fig. 11).

Table 3. Minerals detected by XRD in the LF slags of ÓAM Ltd. (+ means the mineral is present in the slag)

	dissociated	white lumpy	brownish grey lumpy
gehlenite (g)	+	+	+
calcite (c)		+	
merwinite (me)		+	+
larnite (l)		+	
bredigite (b)	+	+	+
mayenite (ma)	+	+	
periclase (p)	+		
spurrite (sp)		+	
Mg-kutnahorite (k)	+		

During the cooling of the slag the presence of larnite makes the slag susceptible of disintegration. This can be explained by the larnite β-γ structural transformation that increases the volume (by aprox. 10%) of the larnite crystal. This structural stress can turn this slag into slag powder (Fig. 1) (Cavalotti et al., 2007). Formation of slag powder has both advantages and disadvantages. Extraction of metal residues from slag powder on the one hand is relatively easy by sieving and electromagnetic separation as crushing is not necessary. On the other hand, fine particles of the fresh slag powder exposed to wind erosion pollute the air. To avoid this, pollution water is sprinkled on the slag powder. The hydrated material makes a bonded solid crust on the sprinkled surface. As a result carbides, sulphides, nitrides, phosphides dissociate while small amount

of acetylene, methane, ammonia, hydrogen sulphide and phosphine are formed that, however, present no health risk.
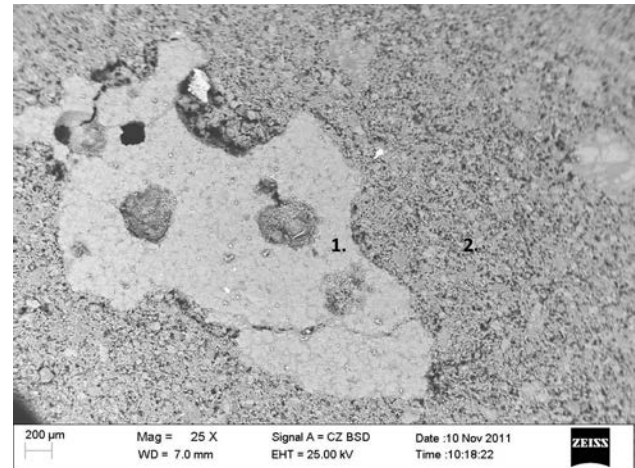
component	1. (wt. %)	2. (wt. %)
MgO	1.25	9.39
Al_2O_3	4.57	7.65
SiO_2	31.19	29.64
CaO	62.47	51.50
MnO	0.52	1.02
FeO	-	0.77

Figure 11. SEM/EDS analysis of secondary slag powder. On the image a slag particle that has not been disintegrated yet (1) can be seen together with the enclosing weathered matrix (2). The table gives the major element composition of the two phases (1., 2.) based on EDS analysis
1. light field, 2. dark field on the EDS image

Air moisture and water sprinkled onto the slag powder create a strong crust on the slag. The material that could be broken easily by hand at the time of its formation becomes very hard in a few months due to the presence of calcium-aluminate and the free lime content. Finally, carbonates (e.g. calcite, aragonite) are formed as well. Various calcium aluminate hydrates are formed out of the calcium aluminate silicates (Ukrainczyk et al., 2007), and different calcium silicate hydrates (CSH) such as spurrite [$Ca_3(SiO_4)_2CO_3$], tobermorite [$Ca_5Si_6O_{16}(OH)$ x4 H_2O], xonotlite [$Ca_6Si_6O_{17}(OH)_2$], jennite [$Ca_9Si_6O_{18}(OH)$ x 8 H_2O], etc. may occur as well (Hong & Glasser, 2004). We have proved the presence of calcite and Mg-kutnahorite (Fig. 12) and the already mentioned spurrite as a complex carbonate silicate.

The presence of Mg-kutnahorite proves that periclase existing in the slags can react with the free metal oxides (FeO, MnO) and also with CaO as they can form solid solution with each other. Thus it seems like the detected Mg-kutnahorite was formed by the

carbonatisation of the solid solution of the oxides mentioned above. The sulphur content may decrease to one hundredth of its original amount as it mostly dissolves out forming mainly various sulphates like gypsum, barite, etc. (Fig. 13). The ratio of slag that was not turned into powder remains generally at 5-10%. This residue is generally saturated and oversaturated by silica and alumina (e.g. brownish grey, lumpy slag).
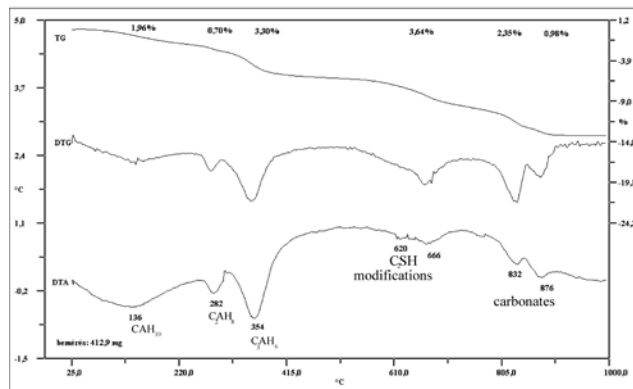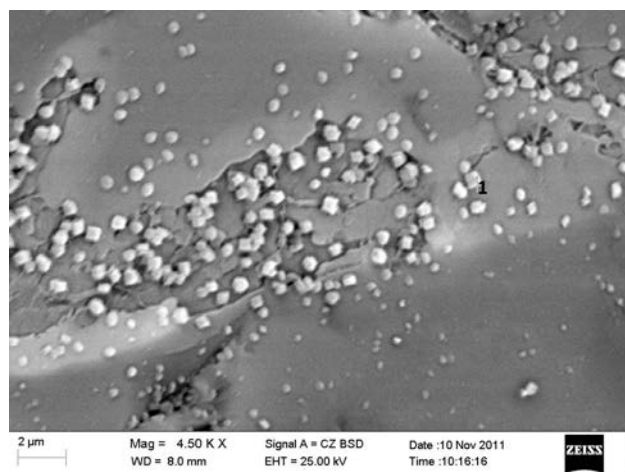

Figure 11. Derivatogram of a one year old, bonded LF slag (OAM Ltd.) (measurement conditions: heating velocity is 10 °C/min using ceramic crucible at atmospheric pressure)

component	1. (wt. %)
Na$_2$O	0.89
MgO	2.34
Al$_2$O$_3$	15.08
SiO$_2$	22.19
CaO	54.81
BaO	1.07
TiO$_2$	0.31
MnO	2.29
SO$_3$	2.50

Figure 13. SEM/EDS analysis of brownish grey, lumpy LF slag. On the image of the surface of the slag secondary mineral precipitations can be seen the major element composition of which are presented in the table based on EDS analysis

3.4 The facilities of slag utilisation

Utilisation of the studied ladle slags is limited because the dissociation of their material starts a long time after their formation, however, it intensifies rapidly once started even if the slags were in a dry place. Solid slag pieces seem to be stable and start to become slag powder after one year. Knowing the process in detail may have benefits considering the utilisation of the slag as retarded slag fertilisers since useful trace elements are exposed slowly and gradually. Side effects of the sulphide content include that it is fungicide. Due to their sulphur content and slightly basic pH these slags can be beneficial to the soil considering the cultivation of brassicacea and fabaceaea plants like cabbage, rape, medick, bean, pea, etc. The trace element content of the slags can be useful as a micro-element fertilizer. Most of the residual trace elements are essential for plants (Loch & Nosticzius, 1992).

Ideal application would be the metallurgical utilisation, because the conditioned slag contains sulphur as a trace element only and its high lime and alumina content make its liquidation easy. Therefore is by-product could be sold following briquetisation or pelletisation and final calcination as synthetic slag for secondary steelmaking. Based on Italian experiments the white slag powder is a suitable slag foaming flux in the process of EAF steelmaking because the blown slag powder together with coke powder form a high number of crystal rudiments increase the stability and cohesion of the foam. In this way high number of large gas bubbles are formed that increase the volume of the slag foam. This slag foam helps to increase the efficiency of heat transfer from the arc to the steel bath. Due to the soundproof capacity of the slag foam, the noise pollution generated by the arc can be reduced (Cavalotti et al., 2007). Adding secondary slag rich in free lime to the system much less amount of slag forming lime will be needed. In this way the cost of steel production can be reduced.

Slag powder has lower melting point than lime therefore it makes basic slag faster than lime and this is beneficial considering refractory lifetime. Sulphur content of the utilised slag powder has to be noted similarly to that of the input steel waste because extremely high sulphur content may occur in the melt without the careful calculation of the input sulphur content. Removal of this would require significant cost and time reducing the profit of steel production.

Non-dissociated, lumpy slags could be utilised in the cement industry as well due to their even

composition and low content of impurities (e.g. S, Mn, K, Na). Applying slag powder reduces the amount of limestone quarrying and input. The material of the slag is suitable for setting the aluminate content of the clinker. Before such utilizations, however, more detailed investigations are required in order to understand the limiting conditions of application. Simplest and most common way of utilisation is using slags mixed with crushed stones in the foundations of roads (Márkus & Grega, 2006).

4. CONCLUSIONS

Ladle furnace slags are susceptible of disintegration induced by the volume change of dicalcium silicate (larnite). This process results in a high quantity of slag powder. In minor amount non-dissociated lumpy slags remain as well due to the fact that the composition of the slag is heterogeneous. The major composing minerals of slags belong to two groups: the gehlenite–akermanite series belonging to sorosilicates and the larnite–bredigite series that belong to nesosilicates. Apart from these, accessory minerals also occur in the slags, however, in smaller quantities. Among them mayenite is the most important. In very small quantities these slags also contain various heavy metals. The most characteristic among them is barium that is mostly precipitated as non-soluble barite in the course of the disintegration of the slag therefore it presence no environmental risk.

Recycling and re-utilisation the above slags are yet to be solved. One way of utilisation could be their return to the EAF to produce and improve the stability of slag foam. In this way, heat transfer towards the steel melt can be improved and the overall costs of steelmaking could be reduced.

Currently the studied slags are used in road construction, however, they could be ideal for soil melioration as well especially where brassicacea and fabaceaea plants are grown.

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