Behaviour of ladle slag minerals in atmospheric conditions regarding utilization

Üstsalak ásványok viselkedése légköri körülmények között különöse tekintettel az alkalmazásra

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Abstract – The secondary steelmaking slags contain numerous minerals such as larnite, Ca-aluminates. The formed ladle slags are unstable in the atmosphere so they are dissociating to fine powder. The modification change of larnite (C_2S) is the main cause of this phenomenon. The fresh formed white slag powder is unprotected against wind erosion. The water sprinkling creates a solid layer on it instantly. We have found that this layer contains calcium aluminate hydrate that causes rapid binding. This protective layer reduces the effects of wind erosion significantly.

Összefoglaló – A szekunder salakok sokféle ásványt tartalmaznak, amilyen például a larnit és a különféle kalcium- aluminátok. A képződött salakok a levegőre kikerülve fehér porrá esnek szét, amit főként a larnit módosulása idéz elő. A frissen képződött fehér salak fokozottan szélerózió érzékeny. Vízzel történő locsolás hatására viszont szilárd kéreg képződik rajta. Vizsgálataink szerint ez a kötött réteg kalcium-aluminát-hidroxidokat tartalmaz, melyek a gyors kötés okozói. E védő burok hatására a szélerózió lehetősége jelentősen csökken.

Keywords – minimill, Ladle Furnace, deoxidisation, oldhamite, calcium-aluminate,gehlenite
Tárgyszavak – miniacélmű, üstkemence, deozoxidáció, oldhamit, calcium-aluminát,gehlenit

Introduction

The first step of steelmaking is the so called primary steel metallurgy. By this way the charged material goes across oxidization. The result of these stages is the uptake of the oxidable nondiserable elements such as Si, Mn, P to the slag phase as SiO_2, MnO, P_2O_5. At the same time the initial S content of the steel decreases significantly (max. 50%) while it is absorbed in the slag. As they use the most common technology, primary steelmaking is very similar at the integrated steelworks, however, it can be different at the minimills. At the integrated steelworks mainly basic oxygen furnaces (BOF) are in operation which consume the hot metal produced by the blast furnace. So at the BOF area the main charging material is hot metal (75%) with well known quality and the rest of the material contains separated scrap (25%), so it contains nondiserable elements in relatively low concentration. In this situation the theoretical probability of „catch carbon heat" technology is given where the heat is under oxygen blasting until the carbon content decreases to the diserable level and then the heat is tapped. The steel produced in this way contains dissolved oxygen in a relatively low concentration resulting in the lower consumption of deoxidants. Nowadays these methods are becoming widespread worldwide. Most of the BOF meltshops use „building up heat" technology that means total oxidation of the batch. Therefore the final product is steel with almost zero C, Si, P, Mn content that is carbonized under tapping, and treated in the ladle. This is a reasonable technology because the steelmakers can produce relatively clean raw steel from contaminated raw-material for secondary steelmaking facilities.

The minimills work with 100% The UHP (Ultra High Power) EAF(is the soul of this mill types. The most applied method is the one mentioned first, the "building up heat" technology. The scrap charge is melted down by the electric arc and oxyfuel jetburners such as in the Steelwork of Ózd Ltd. (OAM Ltd.). By the end of the heating the steel bath becomes oversaturated in oxygen. After casting gases would form eraised hollows as gas inclusions in the rolled steel products that are harmful. Other problems are the high inclusion and sulphur content. These parameters do not meet the requirements of the steel standards

These quality problems can be avoided by secondary refining. Secondary steelmaking technologies can be separated substantially to two types, the atmospheric and vacuum technologies. The mini mill type steelworks to meet this requirement use different ladle metallurgical technology (for example: vacuum technologies: VOD, ASEA-SKF etc) (Szőke 1990).

The most advanced and fundamental technologies are the atmospheric gas purging (AP) technologies where the inert gas (N_2, Ar) flows into the ladle at the bottom of the ladle via a purging plug. The standard technology consists of two technological steps. The first step is the precipitational deoxidation while the steel is under tapping. The next step is the diffusion deoxidation which is carried out in a ladle furnace where the steel obtains its final composition and the inclusions are floating into the slag and there they are absorbed

Mineralogical effects of secondary metallurgy

By the process the EAF getting tap the described quantity of steel, while at the same time the ladle treatment of the steel starts. In this way flux additives and deoxidant agents are given to the steel flow. These deoxidants are ferroalloys (FeMn, FeSi, FeSiMn, etc.) and aluminium. Flux additives are: lime, alumina, alu-slag, fluorspar and coke breeze as carburizing agent. The ferroalloys and the aluminium are reacted with the active dissolved oxygen resulting in dropping down (20ppm) of the initial oxygen content. This technological step is called precipitation deoxidation, where the oxygen forms different oxides and silicates thus precipitating itself. The eraised particles in the bath are different minerals such as fayalite-knébelite-cristobalite, corundum, herczynite, etc. They have different density and grain diameter. This results in the different floating velocity of the slag. This phenomenon can be easily calculated by the formula of Stokes. But the remaining particles are the inclusions of steel. These residual minerals cause the clogging of the wellblock such as corundum and mayenite so the casting becomes disturbed and problematic. The dilatation of the inclusions is different and they cause structural stress resulting in the deterioration of the steel product.

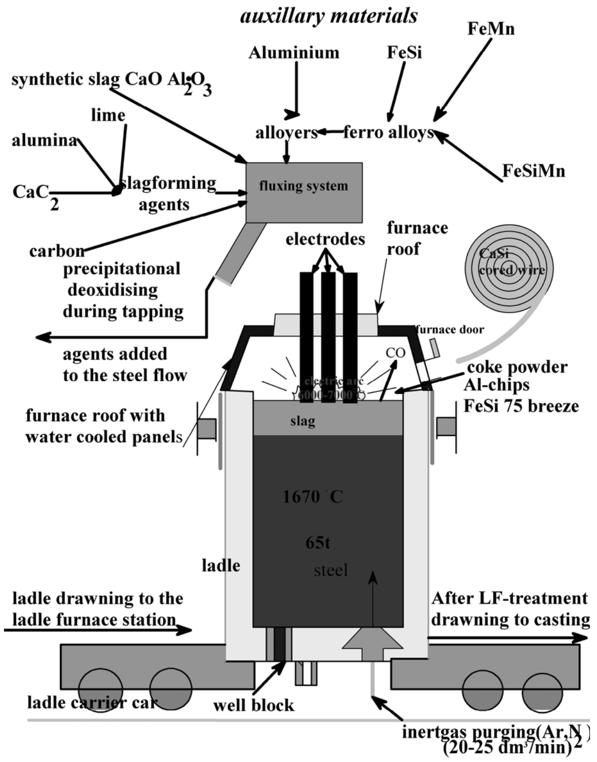

Figure 1: schematic diagram of the ladle furnace at OAM Ltd.

1. ábra: Az OAM Kft üstkemencéjének sematikus folyamatábrája

The function of lime flux are either to absorb these deoxidation products or to transform them to another non harmful ductile inclusion. These compounds are different. The basic slag, the high lime content and the reductive environment perform good desulphurisation (*Figure 2*). In this way the sulphur content of the steel melt is precipitated as metal sulphides such as FeS (troilite), MnS (alabandine), CaS (oldhamite) and MgS (niningerite) floating up to the slag. There are some purging plugs at the bottom of the ladle. The gas purging generates circulation in the melt towards the slag and down to the bottom. In this way – while ladle being transported to the Ladle Furnace stand – the inclusions and other reaction products are floating up and the dissolved gas content (CO, H_2) decreases as well.

Usually three graphite electrodes are set in the melt so they heat the bath until the temperature reaches that the casting needs (*Figure 1*). At the same time, circulation of the melt is continuous and the remaining oxygen content decreases further.

The process last mentioned is the diffusion deoxidation, because the equilibrium of the FeO, MnO concentration in the metal/slag phase is modified. That means lower FeO, MnO concentration is kept in the slag by the addition of deoxidation agents such as, Al, FeSi powder, CaSi and coke powder (SIMON et al. 1980). The reduced metal content of the slag flows into the steel bath.

The desulphurisation is a similar process. Temperature is high (6000-7000°C) close around the electrodes. In these conditions carbides might have eraising (CaC_2, Mg_4C_3, SiC, Al_4C_3 etc.), but hypothetically, different fullerens, metallokarboeders can be eraised to. The added lime flux forms clinker like minerals with the non-decompositive products of deoxidising like corundum and a few silicates.

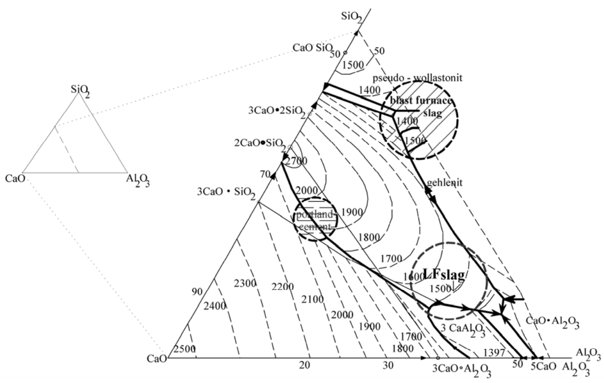

Figure 2: The situation of the ladle slag in the $CaO-Al_2O_3-SiO_2$ ternary system

2. ábra: Az üstsalak a $CaO-Al_2O_3-SiO_2$ háromszögdiagramban

	dissociated	White lumpy	Brownish grey lumpy
gehlenite	+	+	+
lime	+	+	+
merwinite	+	+	+
larnite	+	+	
bredigit	+	+	+
mayenit	+	+	
periklase	+	+	
ferdisilicite	+		

Table 1: The XRD detected minerals from the slag types (analysed by P. Kovács- Pállfy – P. Kónya)

1. táblázat: A salaktípusokban RTG vizsgálattal kimutatható ásványok (elemezte: Kovács-Pálffy P. – Kónya P.)

These are the following: calcium-aluminates e.g. C_2A, C_3A and mayenite, silicates such as C_2S (larnite), C_3S (hatrurite), gehlenite-akermanite, etc. The sulphur content forming MnS alabandine – CaS oldhamite – MgS niningerite – (Fe,Mg,Ca)S kielite series. The precipitated calcium-aluminate grains affect the sulphides as mineralizators, as floating aluminate inclusions adsorb sulphides on their grain surface as oldhamite coatings (SEILEROVÁ et al. 2004).

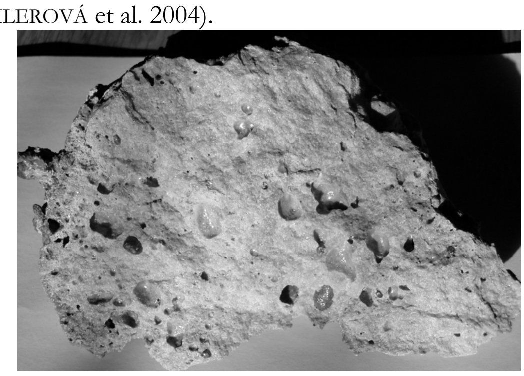

Figure 3: The white lumpy LF slag

3. ábra: A fehér darabos üstkemence salak

We have carried out X-ray diffraction analysis to describe the mineralogical composition of the slag. We have found that the predicted main minerals occur in the investigated slags, except for the hatrurite and spinell. Perhaps they are in the slags but in subcrystal state or they form stable silicates such as gehlenite, bredigite, Merwinite.

Figure 4: The lumpy brownish gray Lf slag

4. ábra: Barnásszürke darabos üstkemence salak

The sulphides form pyro sols and they are dispersed in the slag as colloid scale particles which cannot be detected by XRD method, but the effect of water smells like hydrogen sulphide thus it can be suggested that they are present in the dissociated and in the white lumpy slags as well. We have found ferdisilicite in traces. This originates from residual Ferrosilicon deoxidising agent.

Mineralization of secondary slags

The cooling slag in the presence of larnite tend to disintegrate, that can be explained by the larnite β-γ, structural transformation that increases volume (approx. 10%) of the larnite crystal. This structural stress turns the slag into slag powder. The eraisement of this powder is an advantage and a disadvantage at the same time. The advantage of this phenomenon is the easy metal recycling because metal residues can be extracted by sieving and electromagnetic separation without crushing. Disadvantage of this material is the presence of fine particles because the fresh powder is exposed to wind erosion so it is hard to manipulate this material without air pollution. The most common method of avoiding pollution is water sprinkling. The hydrated material makes a bonded solid bark of the sprinkled surface. Water dissociates carbides, sulphides, nitrides, phosphides while small amount of acetylene, methane, ammonia, hydrogen sulphide phosphine eraises which cause no health risk

The effect of moisture and watering the slag powder is bounded. At the beginning, existing relatively loose material (breakable by hand) solidifies in a few months by the effect of calcium-aluminate (UKRAINCZYK et al. 2007) and free lime content. This process finally forms carbonates such as calcite, aragonite, *(Figure 3)*. The sulphur content is solved out and

LF slags	$-H_2O$ %	$+H_2O$ %	SiO_2 %	FeO %	TiO_2 %	Al_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	MnO %	S %	other (SiC) %	B_3
Dissociated	0.27	-1.03	20.55	1.30	0.05	17.56	48.34	7.27	0.03	0.35	0.32	0.67	3.00	1.46
White lumpy	0.64	-0.49	16.07	0.67	0.03	16.92	55.10	5.83	0.06	0.35	0.00	1.89	2.00	1.85
Brownish Greyish lumpy	0.36	-0.34	25.74	1.11	0.02	20.98	37.97	8.31	0.10	0.34	1.19	**0.09**	3.00	**0.99**

Table 2: The main element composition of the ladle furnace slags

2. táblázat: Üstkemence salakok főelem összetétele

the residual sulphur content is only hundred part of the starting total content. The ratio of the residual non-dissociated material to the total mass is about 5-10% because these material phases are saturated or over saturated in silicon dioxide (SiO_2) and alumina (Al_2O_3) i.e. brownish-greyish lumpy slags (*Table 1*) belong to that group. The definition of basicity is as follows:

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

$B_3<1$ acid $B_3=1$ intermediate $B_3>1$ basic (ideal)

This type of slag is intermediate and slightly acid $B_3=0.99$. It is an inefficient and harmful melt, as it cannot absorb any sulphur but corrodes the refractory lining of the ladle.

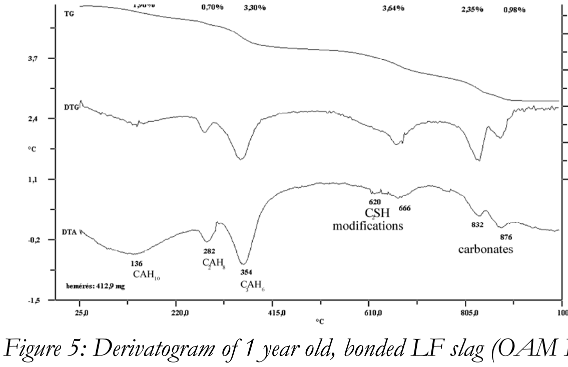

Figure 5: Derivatogram of 1 year old, bonded LF slag (OAM Ltd.) (measurement: heating velocity: 10°C/min, ceramic crucible, air atmosphere

5. ábra: Az 1 éves, kötött LF salak (OAM Kft.) derivatogramja (mérés: felfűtési sebesség: 10°C/min, kerámia tégely, levegő atmoszféra)

Utilization possibilities

Utilization of the above slags is limited, because the dissociation of these materials is very slow and takes place even if samples are kept at dry places the room atmosphere. We have observed that the solid, stable looking pieces of slag kept on air tend to turn into slag powder by "self-powderising" within one year (i.e. white lumpy slag). This process can be beneficial for utilization as retarded slag fertilisers because the useful trace elements are digested slowly and gradually. Its sulphide content can be useful when the material is used as fungicide agent in desirable quantity (LOCH & NOSTICZIUS 2004). The sulphur content and slightly basic pH can be beneficial for the cultivation of brassicacea and fabaceaea families such as cabbage, rape, alfalfa bean, pea, etc.

Ideal utilization of the material is the metallurgical utilization, because the conditioned slag contains sulphur as a trace element and abundant lime and alumina. The product can be sold as syntetic slag for secondary steelmaking after briquetisation or pelletisation and final calcination.

According to Italian experiences (CAVALOTTI et al. 2007) the white slag powder is ideal for slag foaming flux at EAF steelmaking, because the blowed slag powder without coke breeze under the slag forms numerous crystal rudiments that make cohesive foam structure. So the growing number of gas bubbles causes larger slag foam volume. This slag foam helps to make larger heat transfer of arc toward the batch and give good sound insulation capacity, thus noise pollution can be decreased (CAVALOTTI et al. 2007). The most beneficial fact is the lower consumption of lime flux making the budget of production reduced as well.

The pelletisation of the slag powder can be simple. So the handling of the pellets is easier than that of the powders. Pellets can be sold easily as road construction material or in other forms of utilization.

The first mentioned undissociated lumpy slags are valuable for the cement industry because they have saturated composition with low ratio of contaminants (i.e. S, Mn, K, Na) for producing cement. This material is ideal to set the aluminate content of the clinker. It requires, however, numerous other examinations to decide on this type of utilization. The easiest utilization would be to use the material as crushed stone for road construction (MÁRKUS & GREGA 2006).

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