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Selected Aspects of the Assessment of the Quality of Slag

A.W. Bydałek[a,b,*], M. Holtzer[c]

[a] AGH University of Science And Technology, Faculty of Non-Ferrous Metals, Al. Mickiewicza 30. 30-059 Kraków, Polska
[b] University of Zielona Góra, Faculty of Mechanical Engineering, ul. Podgórna 50, 65-246 Zielona Góra, Polska
[c] AGH University of Science And Technology, Faculty of Foundry Engineering, W. Reymonta 25. 30-059 Kraków, Polska
* Corresponding author. E-mail address: adam_bk@poczta.onet.pl

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Abstract

Two approaches have been proposed to analyze the quality of the slag: metallurgical evaluation of and environmental impact assessment. The analysis of the metallurgical quality of the slag using the DTA methods was carried. In the paper a method of determining the reduction capability of slag solutions was used. There are the oxides complexes used in to the slag composition for the purpose to establish two quality indicators in reduction processes: EW - indicator showing the direction and intensity of reaction in to the slag composition and r - indicator of the rate of coal consumption. Proposed to other qualitative criteria. The analysis was conducted on the example of slag from aluminium metallurgical processes, and slag from the smelting processes of copper and its alloys. Divided influence on the environment and the use slag in other processes. Discusses the quality of the slag as a function of their operating qualities. Highlighted the need qualitative assessment of slag in a broad sense. Indicated the necessity to analysis including the quality of the slag more criteria, including: - technology - suitability for further processes, - operational, environmental and economic benefits.

Keywords: Slag quality, Reduction capability, Environment

1. Introduction

In the existed considerations it has been indicated repeatedly that there is a necessity to analyse a real metallurgical system together with all the interactions occurring in it. In order to carry out such an analysis trials have been undertaken to estimate refining efficiency of complicated sets of reagents in real industrial systems.

The ideal orientation of any metallurgical process is a "zero waste". This is when the process not generated the waste. This is possible when all the reaction products are suitable for sale. This concerns both the main product (metal) and the products (slag). The process quality is designed such that the products of reaction occurring (which could be considered to be waste) are processed into useful products. This is a step in the direction of sustainable development. Another object is to generate waste environmentally friendly.

With respect to slag, there are two focus: - the slag should be directly directed to the production of steel within the plant, or to the recipient of slag processing the finished product - such as a filler construction elements. Thus, the primary criterion of quality in relation to the slag should be the elimination of storage. The second criterion is the indifference of environment, in relation to which apply the relevant legislation. The extractive metallurgy slag phase is generated mainly from entering mixtures of oxides and fluxes and also may consist of reaction products, such as oxidation of the metal charge and dissolution of the refractory lining.

The proposed new quality criteria will be discussed on the example of metallurgical slag from the processes of aluminum and copper metallurgy.

2. Assessing the refining abilities of slag through modeling a real process of metal melting

Two melting stages have been specified in the analysis of metallurgical changes for real conditions of slag refining of copper alloys [1-3]:

- heating the metallic charge of a solid state
- meltdown and overheating of liquid metal alloy.

The division explains the necessity of the analysis of the whole system starting from ambient temperature up to alloy melting points. Taking into consideration the characteristic of the metallurgic processes the latter stage, in which diffusion processes are considerably accelerated, should be recognised as the most influential. The established (Fig.1) conditions of the metallurgic process in the hearth furnace required creating a similar empirical system, which with the use of a thermo-differential method, will allow monitoring all the changes taking place. A refining alloy has been replaced with the a mixture of oxides occurring in the metal bath as a result of interactions with melting atmosphere and other accidental factors of metallurgic processes. The oxides were introduced in the amounts and mutual proportions corresponding with melting losses of the tested alloy. They are marked with WN. The metal drops, registered during the structural investigations, made the interaction conditions similar to the ones in a real system. By analogy to real conditions (Fig.1) the remaining external factors were taken into considerations in the model system of melting in to the reduction conduction [2-5].

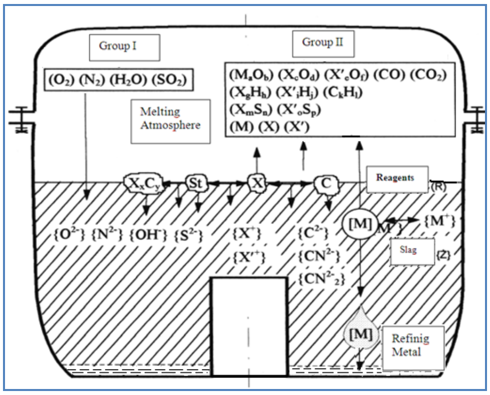

Fig. 1. A proposed model diagram of refining process of a liquid metal with a Carbo-N-Ox slag solution [3]

The factors referred mainly to the temperature rising in time and limited influence of external atmospheric factors (the cover on the measurement crucible), where:

I - components of the furnace atmosphere such as: oxygen, nitrogen, water vapour, sulphur oxide, etc.

II - gaseous products of the reaction of agents from group I with the components of refining cover or metal vapours.

Mutual interaction in the discussed slag model system between active reagents as well and oxides of refined components of alloys was analysed through tracing/investigating thermal and mass effects in function of temperature rising linearly. It corresponded with the previously made assumption of the advisability of evaluating the changing in time interactions during an overall technological cycle [2-5]. The analysis of slag containing WN allowed to establish the possible combinations of EW and r values (Figure 2) together with a proposed explanation. On the basis of calculations it was also found that due to the differences in vaporisation or reaction with the atmosphere of compositions the simultaneous consideration of two values (r and EW) is necessary – Tabl 1.

Table 1.
The explanation of results on the basis of indicators EW and r [4]

	Value of "EW"	Size of "r"	Explanation
1	EW << 0	r << -10	strong reductive interaction
2	EW << 0	r∈(-5, -1)	weak reductive interaction
3	EW ≤ 0	r∈(-1, 0)	no reductive interaction
4	EW > 0	Any r	oxidizing reaction

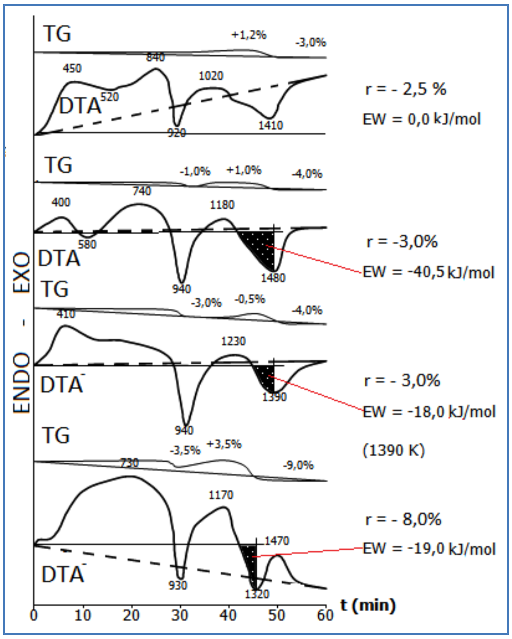

Fig. 2. An example of analysis of the quality of the slag for their ability refining - the DTA/TG diagrams for the bronze melting conditions with the indicators EW and r (different slag)

3. Evaluation of quality of slag due to the impact on the environment

3.1. Evaluation of quality of scaling of aluminum production process

Slag treatment. A slag treatment of Aluminum and its alloys is only necessary when very fine particles like chips are molten [6-9]. The natural Aluminum oxide skin prevents the burning of Aluminum melts up to 700°C. In Aluminum recycling where fine fractions are molten usually salts on the basis of sodium chloride and potassium chloride are used. The mixture depends on the local deposits and suppliers. This system is selected, because the melting temperature is close to the melting temperature of Aluminum but at the same time the system has a rather high evaporation point. This mixture has a better wetting behaviour for oxides that for Aluminum metal and therefore takes up oxides during a melt treatment and last but not least it is readily available and cheap. Usually to the salts on chlorine base fluoridic compounds like AlF_3 or CaF_2 etc. are added. The fluorides accelerate the cracking of the Aluminum oxide layer and therefore improve the coalescence [6].

One of the products (ie. By-product) for production of aluminum is mill dross. It is assumed that the processing of 1000 mg of aluminum scrap is achieved 760 secondary aluminum Mg, 240 Mg mill dross and 3 Mg of dust. In these processes, the quality of slag can be determined on the basis of their suitability for further processes.

In to the aluminum metal industry, there are three types of dross [13]:

1 - white dross - resulting in the production process of primary aluminum foundries, with die-casting, rolling mills, extrusion installations. The main element of quality is related with the presence of aluminum oxide. This can be controlled through the use of an atmosphere containing no oxygen. Two basic methods of treating dross is white; separation of aluminum from dross residue in a hammer mill and melting in rotary kilns under cover of salt.

2 - black dross formed at the secondary aluminum smelting in to the furnaces for melting scrap fiery castings, cans, chips. In these furnaces use as fluxes potassium salts to reduce the possibility of oxidation of the metal. Qualitative criterion will be the slag fluxes. Recovery is only 12-18% of flux. Dross contain 20-50% and 40-55% oxide fluxes of chloride. Several methods are used of dross processing black and salt cake to recover the components contained therein such: physical separation methods hydrometallurgical and pyrometallurgical methods.

3 - "salt cake" - recovery of aluminum with white and black of dross is carried out in rotary kilns under cover of molten salt. The main criterion of quality are salts. This residue containing 3-5% metal oxide 15-30% and 50-75% chloride is called "salt cake" and is stored at a landfill

Salt fluxes used in the treatment of salt slag generated of dross, which is intended for the storage of waste. Therefore, it is necessary to develop a method for the recovery of salt slag waste to reduce the burden on the environment [Table 2.].

Table 2.
Examples of the results of the leaching of aluminum of dross - the impact on the environment [6,7]

The parameter, element	Aluminum dross (metallurgical process)		Aluminum dross (plastic forming)	
	Unit	Value	Unit	Value
The pH	pH	6,2	pH	9,0
Chloride	g/l	2,0	g/l	0,25
Sodium	g/l	1,1	g/l	0,20
Potasium	g/l	0,6	g/l	0,07
Fluoride	g/l	0,16	g/l	0,07

3.2. Slag quality from copper metallurgical processes

3.2.1. Melting of copper and its alloys

Slag by melting copper alloys containing alloying elements [6, 9-11]. Brass melting slag contain Cu, Zn and Pb. Slow cooling of slag results in the formation of various novel compounds: silicates, oxides of nickel and cobalt, Cu_2S, CuS, Cu_3FeS_4 and metallic copper. Reclamation of metals and minerals from the slag from the melting of copper and brass can be done in three ways: flotation, leaching and roasting.

Slag also contain chlorides and fluorides, the amount depending on the adopted technology. In the technology involving neutral or oxidizing slag are between 3-5%, reducing technologies, such as Carbo-N-Ox [2-4] is less than 1%. The presence of these compounds should be a quality criterion [14] due to:

- produced in connection with the carbon dioxin factors - what causes air pollution,
- transition through the hydration of the soil chlorides and fluorides.

3.2.2. Metallurgical production of copper

The basic criterion for quality slag from copper and its alloys be present in them of valuable metals like gold, silver, lead, iron, antimony, arsenic, cobalt. The basic components of copper slags are iron and silicon, each of about 25-50%. Almost all copper slag contain 0.4 -3.7% copper, which is close to or even more than in the copper ores. Slag in copper refining have the task to take up the impurity oxides, formed during the oxidation procedure [12].

High quality of the slag is related to these processes operating criteria. Their properties should be:

- high solubility for impurity oxides,
- low solubility for copper and copper oxide,
- melting temperature close to the melting temperature of copper,
- high thermal stability,
- low interaction with the refractory material

Also investigated by researchers [6] were salt slag that are mainly based on sodium carbonate (Na_2CO_3) but also on other alkaline carbonates like lithium carbonate (Li_2CO_3) and potassium carbonate (K_2CO_3) or other such lanthanides carbonate, chlorides or fluorides. They are very effective refining slag, but they all attack “usual” refractory of the copper industry. It was found that by fluxing with a Sodium carbonate slag the amount of arsenic and antimony could be lowered below 0.1 ppm. This shows the need to take into account the effect of quality criterion as the critical element content.

The problem that occurred was, that the binary solution of Sodium carbonate and antimony oxide let to an increase of solubility of Copper oxide in the slag and therefore to high Copper losses [7, 13,14]. For fluxes on other salt base mainly fluorides can be suitable because their melting and evaporation point is very high. Here especially systems based on calcium fluoride (CaF_2) mixed with aluminium fluoride (AlF_3) or Sodium fluoride (NaF) are possible candidates. All fluxes operate in the best way when the reaction surface between metal and slag is increased for example by solid flux injection in the metal melt [8] instead of an addition to the surface. These considerations point to the environmental quality criterion - the presence of leachable chlorides.

4. Conclusion

The paper quoted an analysis demonstrating the need for making a qualitative assessment of the slag in a broad sense. Is paid attention to:

- analysis of the quality of the slag for their refining ability - the DTA/TG diagrams with the indicators EW and r,
- criteria for technology related to the extractive properties of slag,
- the quality of slag on the basis of their suitability for further processes,
- the quality due to the operational aspects occurring during the manufacturing process,
- environmental criteria, including those associated with the atmosphere and groundwater contamination,
- qualitative criteria including cost due to the presence of critical elements or alloying.

The message of the study is the thesis that it is necessary to take into account all the possible criteria for the determination of the quality of the slag.

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