

DEVELOPMENT OF NEW REFINING SLAG BY PROCESSED INDUSTRIAL WASTE

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Abstract

Fluorspar is the commercial name, currently used in metallurgy. Usually it refers to crude or beneficiated material that is mined and (or) milled from the mineral fluorite (calcium fluoride, CaF₂). From the point of view of ecology and working conditions, the use of fluorite as a slag-forming material causes very harmful fluorine emissions into the atmosphere. From the point of view of technology, it helps to reduce the viscosity of slag by liquefying it on one hand side, however increases the aggressive effect of slag on the refractory lining and shortens its durability on other hand side. We should remember, that the circular economy model (CE) relies on the fact that materials used in production circulate rather than become waste. That's why, the authors of this article want to develop a new generation of materials - synthetic slag based on by-products from the production of ferroalloys. For this purpose, post-production slag, rich in Al₂O₃ and CaO, and some modifiers were used to correct the chemical and mineralogical composition, as well as to reduce the melting point of the developed refining mixtures. The chemical and thermodynamic aspects, were another advantage of developing such slags, because in the case of slag liquefaction via used calcium aluminates, the refining slag remains liquid for a long time, not only for a limited period of time, as is the case with CaF₂ liquefaction. The use of two newly developed slags during secondary metallurgy treatment in steelmaking processes will allow to eliminate the use of fluorite (CaF₂), which has many drawbacks. One of them is the negative effect arising outside the steel production, namely in the process of recovery of zinc from steel dust in the electrolytic process. The presence of fluorine in zinc-rich dusts collected on filters makes zinc recovery difficult. The elimination of fluorite will also reduce the fluoride content of steel dusts destined for zinc recovery.

Keywords: Recycling, circular economy, elimination of fluoride, refining slag

1. INTRODUCTION

The huge rise of the prices of energy sources, increased requirements and stricter regulations in environment protection, as well as economic factors related to the operation of industrial equipment, have made enterprises look for new solutions and take actions to improve the production processes, extending the use of recycling, which in turn will reduce the costs generated by industrial enterprises [1]. Undoubtedly, steelmaker employees should not forget also about the influence of refractory linings on the prime cost of production of 1 ton of steel [2]. On the other hand, Entrepreneurs in the steel industry face rising CO₂ production costs, as well as, the

requirements for waste have been more and more rigorous. Moreover, we should note, that the development dedicated of circular economy is already not news. It's a necessary reality.

Nevertheless, it should be noted that metallurgical slag properties have a great impact on the production efficiency and quality of the smelted steel. Its functions are diverse and vary depending on the type of species fused, the technological process used and the technological period. The steel secondary treatment remains one of the most important technological operations in the steel smelting process. That's why, this technological operation requires a strict approach, namely, increasing the quality of steel refining, reducing the cost of this procedure, reducing the time spent on refining, improving the steel desulfurization process, as well as expanding the range of raw materials. It is worth noting the importance of slag's liquefaction problem via various additives. To a large extent, the refining ability of slags also depends on their liquid mobility, since the processes of desulfurization and deoxidation develop at the slag - steel boundary. At most enterprises, fluorite (fluorspar) CaF_2 is used to liquefy slags, which is an environmentally hazardous substance, has a high cost and aggressively interacts with the lining of the steel ladle. From the point of view of technology, on the one hand, fluorite, helps to reduce the viscosity of slag by liquefying it, on the other hand, it increases the aggressive effect of slag on the refractory lining, shortening its durability. Due to the chemical composition, the resulting refining slag remains liquid for a long time, and not only for a limited period of time, as is the case in the case of liquefaction with CaF_2 , when after the fluorite has evaporated from the slag, it again solidifies. It should also be added that in the case of slag liquefaction with CaF_2 , the interaction with SiO_2 in the slag produces the harmful compound SiF_4 , and with it the fluorine escapes from the slag and the slag thickens again. Failure to use the "time window" in which the slag is liquefied reduces the quality parameters of the steel or the need to reintroduce fluorite, since active liquid refining slag is a prerequisite for the production of high-quality steels with low sulfur content and undesirable inclusions. From the point of view of an ecology and working conditions, the use of fluorite as a slag-forming material causes very harmful fluorine emissions into the atmosphere. It should be noted that the use of fluorite (CaF_2) in European Union is prohibited, due to emission standards (harmful emission of fluorine into the atmosphere) [3] and dust pollution resulting from the process of off-kiln steel processing, which consequently prevents the use of these dusts as a secondary aggregate in the process of recovery of zinc from steel dust in the electrolytic process [4]. At the same time, the issue of elimination of fluorite as a harmful substance in steelmaking remains unresolved [5]. Some researchers have noted the positive effect of Al_2O_3 on the liquid mobility and sulfur absorption capacity of refining slag [6-9]. At the same time, steelmaker's employees should also ensure proper desulfurization of steel [9-10]. This is why the present investigation is devoted to precisely an complex issue.

2. THE ANALYSIS OF WASTE BY FERROALLOY / RAW MATERIALS OUR PRODUCTS



Figure 1 Two types of solid slag made ferroalloy Industry

The achievement of the ambitious goals of this work was preceded by a thorough, accurate and precise waste analysis. For this reason, several studies were conducted: grinding of slags (**Figure 1**) in a 50 kg capacity mill. The Retch 400 planetary mill, equipped with relevant metal and ceramic containers, was utilized for this purpose. At the second stage, X-ray fluorescence spectrometry (XRF) and X-ray diffraction (XRD) analyses were conducted to determine the chemical and phase composition of the slags (**Table 1 and 2**).

Table 1 Chemical composition of two various high aluminate slags

mass %	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	Fe ₂ O ₃	Mn ₂ O ₄	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	V ₂ O ₅	Cr ₂ O ₃	SrO	ZrO ₂
slag No. 1	82,2	0,28	9,72	0,11	0,53	0,01	0,11	0,56	0,06	0,01	0,09	1,11	0,02	0,02	0,01
Slag No. 2	78,9	0,17	2,00	19,6	1,06	0,11	2,24	0,07	0,01	0,03	0,00	0,00	0,03	0,00	0,07

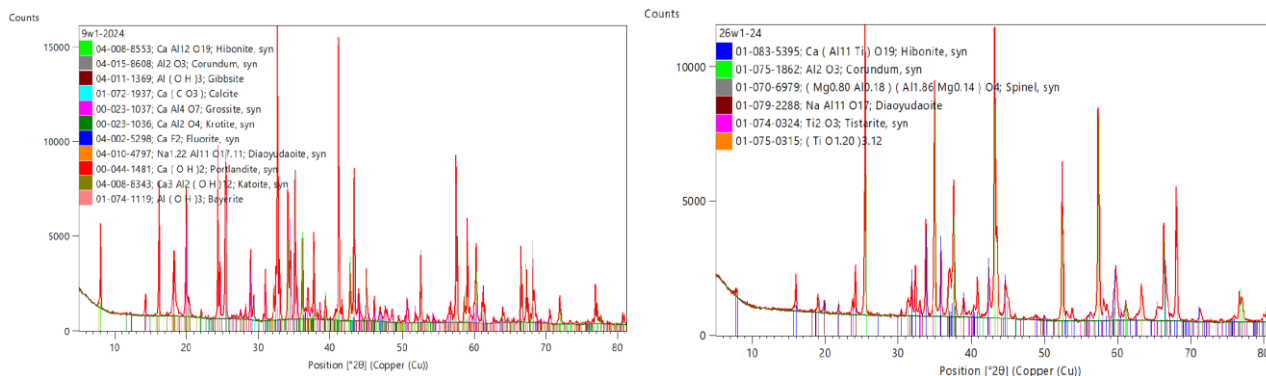

Figure 2 XRD analysis results of the slag, 9w1-2024 – sample of slag No. 1; 26w1-24 – sample of slag No. 2

Table 2 X-ray diffraction analysis - qualitative and quantitative phase slag's composition

Phase composition	Slag No. 1		Slag No. 2	
	Quantitative share, %	Standard deviation, %	Quantitative share, %	Standard deviation, %
Corundum	26,5	0,5	58,3	0,5
Hübnerite	28,9	0,5	22,1	0,4
CA ₂ (Grossite)	28,0	0,5	-	-
CA (Krotite)	0,7	0,3	-	-
Calcite	2,7	0,3	-	-
Gibbsite	10,8	0,7	-	-
Fluorite	0,7	0,1	-	-
Alumina, beta-	0,3	0,2	2,6	0,3
Katoite	0,7	0,2	-	-
Bayerite	0,7	0,3	-	-
Spinel	-	-	9,7	0,3
Ti ₂ O ₃	-	-	2,4	0,2
Titanium monoxide	-	-	4,8	0,1

The authors conducted a detailed analysis of the above-described slag compositions. Taking into account the quite various phase compositions of slag and the presence of phases with high melting point, the authors decided to conduct additional research (**Table 3**).

Table 3 Refractoriness of waste slags

Slag number	Refractoriness, °C
No. 1	> 1770
No. 2	> 1750

Taking into account the quite high temperature of melting of these slag, were conducted the 15 different mixes trials, which contained corrected raw materials. However, this was preceded by several FactSage study simulations (**Figure 3**).

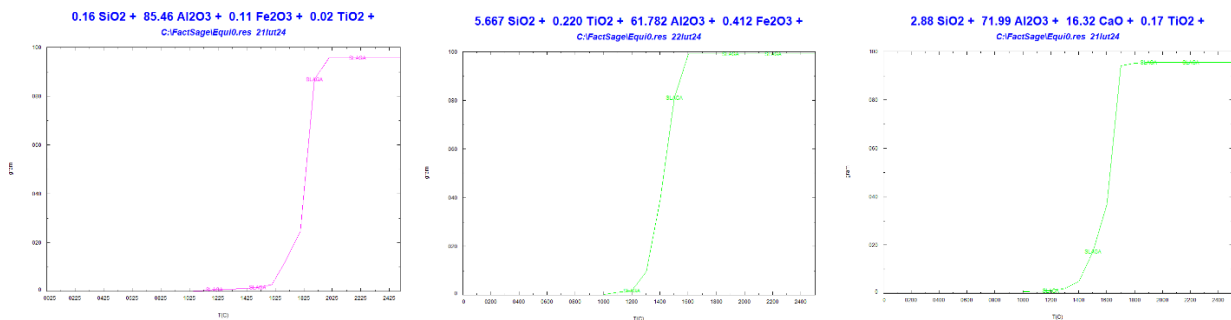


Figure 3 Melting temperature simulation of waste slags via FactSage program

3. LABORATORY TRIALS ON THE USE OF NEW REFINING SLAGS

The next step was to carry out preventive melting in an induction furnace with a volume of 5 kg. The chemical composition of the blend is presented in **Table 4**. The weight of the metallic blend was 2,87 kg.

Table 4 The chemical composition of steel blend No. 1

Element	Fe	C	Mn	Si	P	S	Al	Cr	Ni	Cu	Ti
Mass, %	99	0,02	0,04	0,06	0,004	0,38	0,054	0,04	0,04	0,05	0,0007

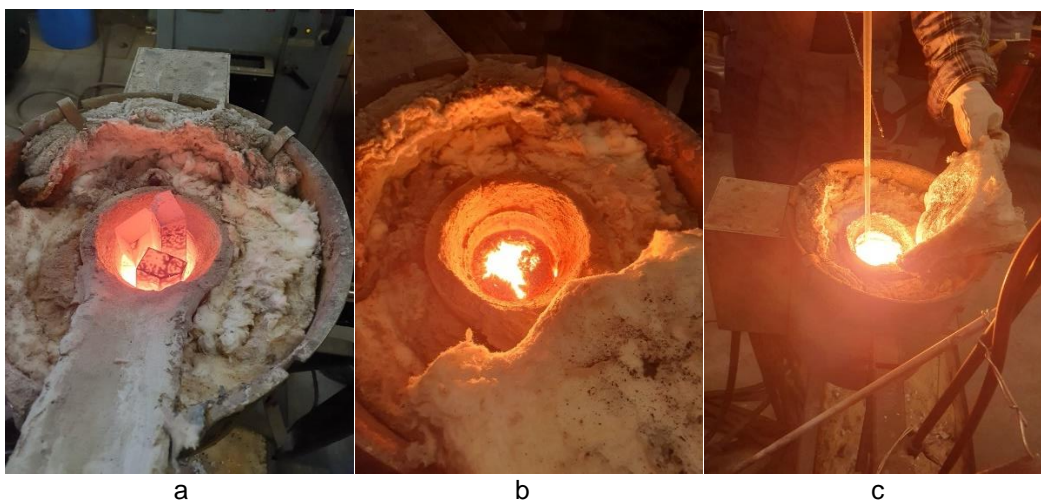


Figure 4 The melting and desulphurization process with use new refining slag: a – the melting of blend; b – thick slag before added refining slag; c – sampling after liquefaction and refining process

This melting No. 1 was conducted without a protective atmosphere (**Figure 4**). The process of steel desulfurization was carried out due to added refining slag with a content: quicklime, mixture slag 1 and slag 2 in X proportion, quartz send and X modifier. We should note that the melting was successful and the slag was very liquid, which prompted the authors of this article to an increase in the basicity in the second melting. Next melting (**Figure 5**) was carried out in an argon atmosphere. The chemical composition of the blend is presented in **Table 5**. The process of steel desulfurization was carried out due to added refining slag with a content: quicklime, mixture slag 1 and slag 2 in X proportion, quartz send and X modifier No. 2. The weight of the metallic blend No. 2 was 3,01 kg. The slag was slightly less liquid (this is how it was designed), but sufficient for successful refining, which is confirmed by the high desulfurization rate (from 0.5 to 0.31%).

Table 5 The chemical composition of steel blend No. 2*

Element	Fe	C	Mn	Si	P	S	Al	Cr	Ni	Cu	Ti
Mass, %	99,1	0,02	0,04	0,06	0,004	0,5	0,054	0,04	0,04	0,05	0,0007

* The metallic manganese, which weighed 15 g was added to blend No. 2

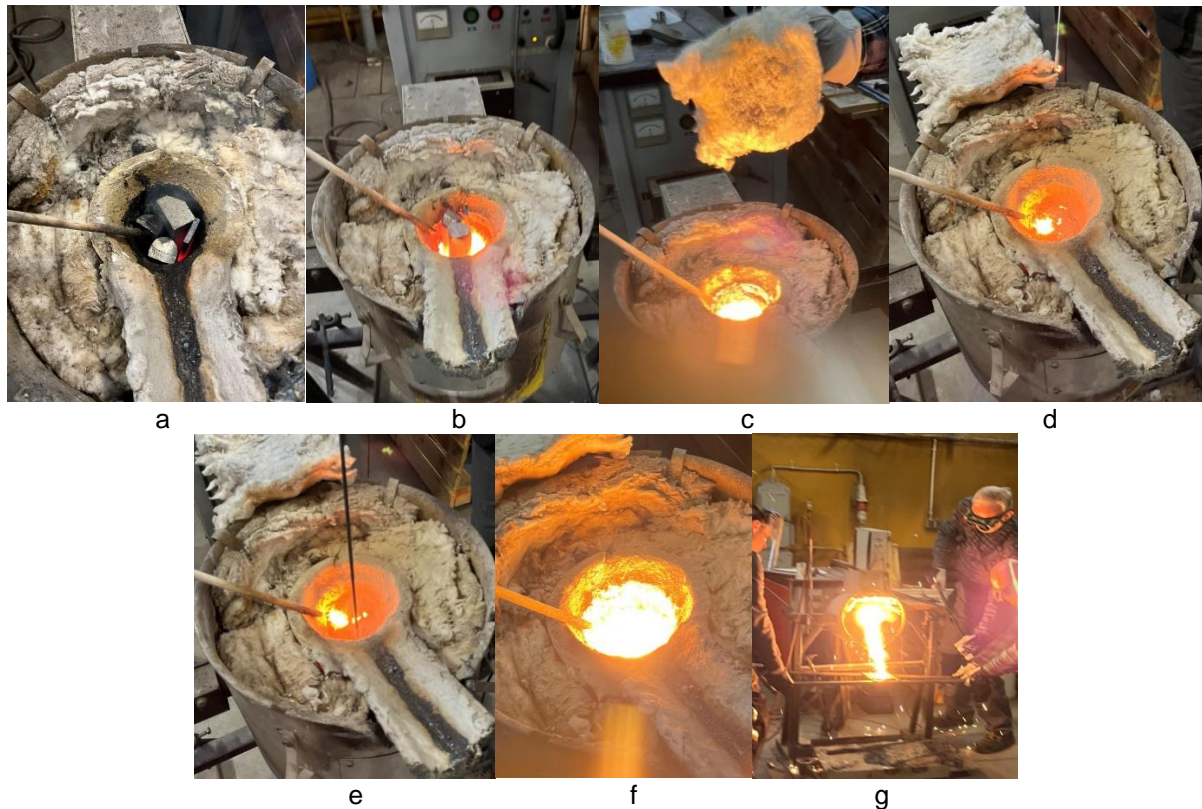


Figure 5 The melting No. 2 in an argon atmosphere and desulphurization process with use new refining slag: a – melting start; b – the melting of blend; c – melted blend; d - the process of an addition of refining slag; e - waiting process for melting slag after added refining slag No. 2; f – the melted slag after added refining slag; g – the steel's drain

4. CONCLUSIONS

1. The experimental researches conducted in this investigation allowed two types of new refining slags for liquefaction of ladle slag. To achieve this purpose, for the first time, were used waste material, which consist of one hundred percent of waste materials by the ferroalloy industry.

2. It has been experimentally proved that the use of calcium aluminate slag in conjunction with other modifiers allows to achieve two maximum effects: satisfactory liquefaction of slag as well as conducted of necessary values of the sulfur index in steel.
3. This development allows to abandon the harmful fluoride materials during secondary metallurgy.
4. Use of new received types of slag, namely the dust and gas after their melting, allows to solve the problem in the process of zinc recovery from dust, which was collected on the filters during the melting process.

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