

VALORISATION OF EAF SLAG THROUGH A DEFINED REDUCTION METHOD

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Introduction

The use of black EAF (Electric arc furnace) slag in road construction and earthworks has a long tradition. Good physical properties and meeting the environmental limiting values lead to a beneficial substitution of natural stones. However, future changes in legislative regulations in Germany¹ could jeopardise the common use of slags in those applications, so improvements to modify the slags must be developed to keep these markets. The most effective way to do this is to treat the slags metallurgically in liquid state and change their chemical and mineral composition. While complete reduction leads to several disadvantages of the produced slag (compromised physical properties) and metal (high P-content), a reduction method was developed to valorise the slag and identify also new applications.

The innovative idea is to use the energy content of the slag for the reduction and to create a special mixture of reducing agents to have a self-sufficient energy reducing process. The reduction rate of the EAF slag must not be 100%, to prevent the disadvantages, as described above. So, a defined reduction grade must be found. To simulate this step, several thermodynamic calculations were performed.

Thermodynamic calculations

The computations were done using ThermoCalc software package. In addition, a closed system was considered in calculations. The fractions of obtained phases and their compositions during the reduction of typical Georgsmarienhütte (GMH) EAF slag (≈ 30 wt% FeO_n and 0.4-0.7 wt% P_2O_5) by carbon addition at 1600°C as well as the carbon and phosphorus contents of metallic product at the saturation were predicted by calculations. To verify the calculations, laboratory trials in a carbon

crucible were performed, which was heated up by an induction furnace. The produced amounts of slag/metal were determined, as well as chemical compositions.

According to the calculations, the content of iron oxides in the slag decreased to below 1 wt% by addition of more than 8 wt% C (6667 moles). Simultaneously, an increase of CaO and SiO₂ with carbon addition has been predicted by calculations indicating the formation of calcium silicates. In addition, significant reduction of phosphorus oxides takes place and it can be clearly observed by enrichment of metallic phase on P with carbon addition (Figure 2). The release of up to 20 wt% of gas phase that consisted of 98.5% CO was predicted by calculation. The C saturation limit in metallic phase is calculated to be 6.19 wt% (Figure 2). According to the calculated results, C saturation occurs by addition of 11.5% C into the reaction bath (Figure 2) which simultaneously leads to the formation of more than 35% of metallic phase.

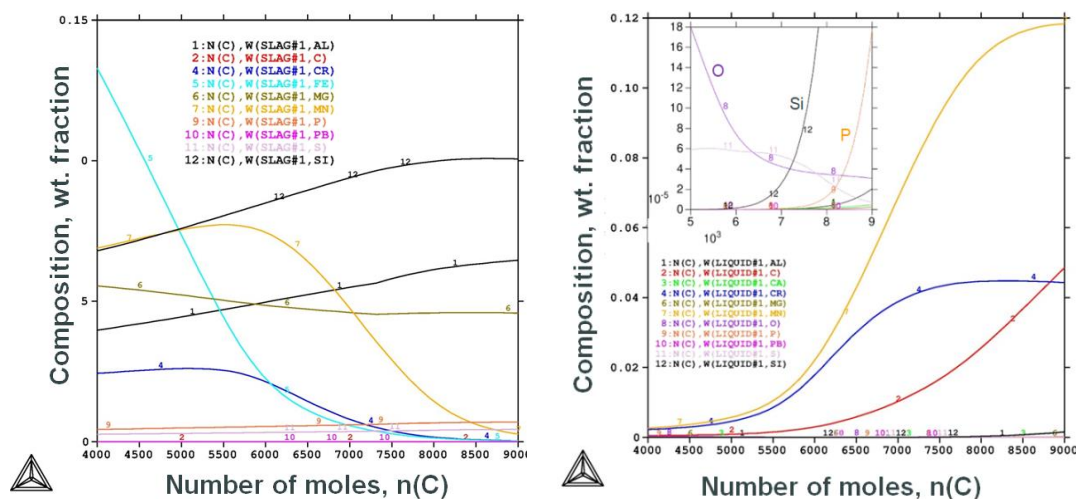


Figure 1: Effect of carbon addition on composition of slag/oxide (left) and metal (right), based on 1 t of treated slag

On the other hand, the experimental set-up leads to an early saturation in C which occurs at a significantly lower amount of added C. It is believed, that due to the use of C-crucibles, that the metallic phase is “immediately” saturated in C (i. e. at first formed metallic drops). Therefore, the metallic phase/slag interface takes a significant role in the reduction reaction. The significantly higher phosphorus content of the metallic product ($\approx 0.4\%$) is experimentally obtained in comparison to the calculated one at the saturation (600 ppm, based on 1 t of slag. See Figure 2.).

However, these findings are reasonable when taking into account that the closed system and the controlled C addition were considered in calculations. On the other hand, the experiments were performed in an open system (the formed gas phase

continuously leaves the system) and using the C-crucible (the presence of C in excess). Therefore, the reduction is continuously carried out for a certain time which leads to a more intensive reduction of phosphorus oxides at lower contents of iron oxides.

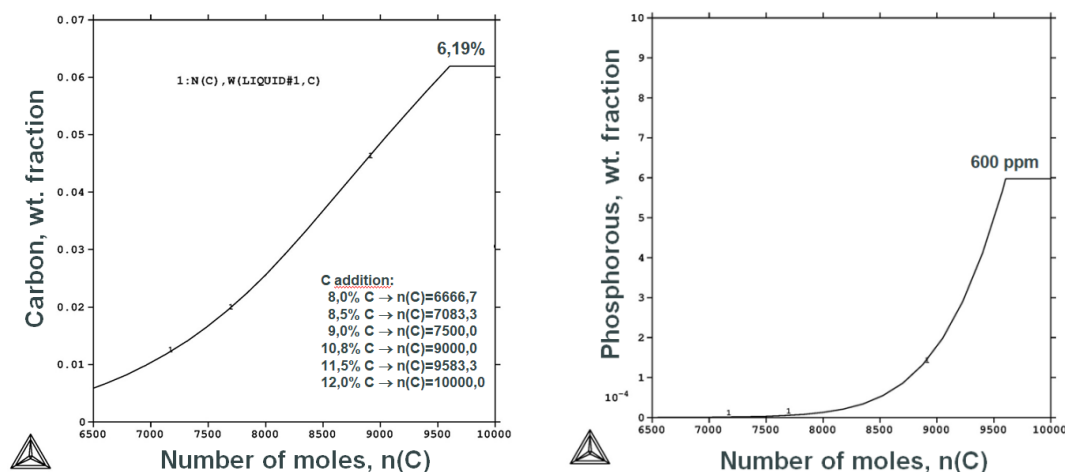


Figure 2: Carbon (left) and phosphorous (right) content of metallic phase at 1600°C

To achieve a satisfactory slag reduction along with lower P contents in metallic phase, the mixtures of selected reducing agents such as Si-based reducing mixtures have been added into the reaction bath. In addition, the laboratory experiments were performed for shorter times in order to limit C entering the system from the crucible while the plant trials were done in the slag pots covered with oxide-based refractories.

Plant trials

To verify these tests in steel work, an injection lance was put directly under the furnace. During slag tapping, the mixture of reducing agents was injected into the liquid slag, to force a homogenisation without any mechanical or electromagnetic stirring. The set-up is shown in Figure 3.

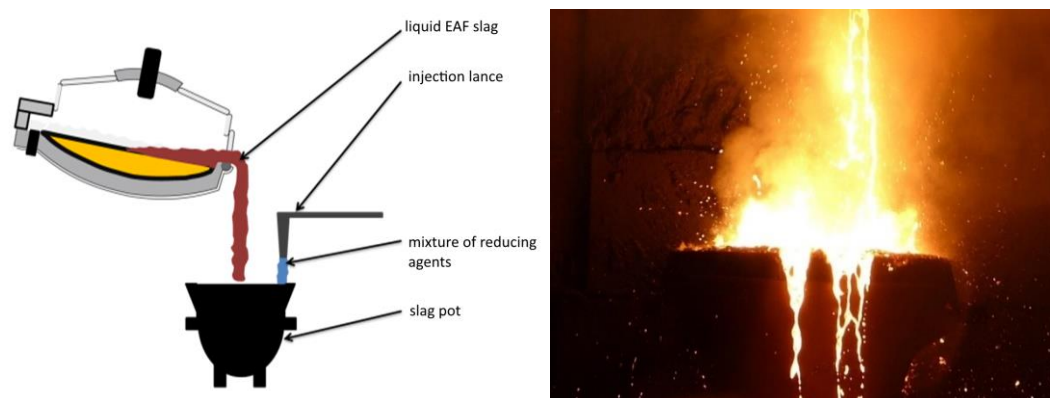


Figure 3: Scheme (left) and photo (right) of the set-up at Georgsmarienhütte

More than 20 tests were performed by this procedure to get statistically firm results. After treatment, the slag was cooled down in the slag pot, so metal pieces inside the liquid slag segregated at the bottom of the slag pot to a metal scull. This method is a logistic and economic challenge for the steel work, due to the need of several slag pots and space.

Quality of products

The described disadvantage of high phosphorous in the reduced metal was prevented. While a complete carbon reduction leads to a phosphorous content of 0.42 wt% on average in the metal phase, it was possible to decrease it to 0.06 wt% by defined reduction method (Table 1). Up to 20 wt% of EAF slag was recovered as metal scull.

Table 1: Mean values of metal composition by complete and defined reduction

	C	Si	Mn	P	Cu	Sn	Cr	Mo	Ni	V
	(wt%)									
Complete reduction	6.0	0.22	6.04	0.42	0.03	0.002	3.6	0.01	0.03	0.24
Defined reduction 1	0.4	5.0	1.2	0.10	0.14	0.011	0.85	0.03	0.09	0.04
Defined reduction 2	1.37	7.0	4.1	0.09	0.14	0.006	1.20	0.05	0.07	0.10

The slag composition before and after reduction is shown in Table 2.

Table 2: Mean values of slag composition by complete and defined reduction

	CaO	SiO ₂	MgO	Al ₂ O ₃	Cr ₂ O ₃	FeO	Fe ₂ O ₃	MnO	P ₂ O ₅
	(wt%)								
Complete reduction	43.7	22.7	14.0	12.6	0.19	0.28	0.18	4.08	0.11
Defined reduction 1	23.1	20.7	8.98	8.9	2.08	15.1	2.4	7.72	0.37
Defined reduction 2	26.8	24.0	9.10	8.41	1.49	10.9	2.96	8.16	0.39

Beside the metal recovery, there is another important aspect for the treatment: the environmental compatibility of current and upcoming regulation. Beside the new parameter molybdenum, also the leaching test changed from shaking test with water/solid ratio (w/s) of 10/1² to shaking³ or up-flow column test⁴ w/s of 2/1. After treatment the partly reduced slag fulfils all requirements of SWS-1 of upcoming regulation. The slag fits also to all requirements of current regulation, see Table 3.

Beside the environmental aspects, the slag with much lower iron oxide content changes also its physical properties. So parallel physical properties like impact test, steam test, *etc.* were also investigated to prevent a disadvantage in marketing of the product. The physical properties were better by trend, but a *regular* crusher is not

sufficient for this kind of slag, due to the very high hardness. Thereby the produced grain size distribution doesn't fit the requested grain sizes for the markets.

Table 3: Results of treated EAF slag

		Slag 1	Slag 2	Regulations			
	Leaching shaking test w/s 10/1 (8/11 mm)			SWS-1	SWS-2	SWS-3	
el. conductivity	µS/cm	128	180	1500	1500	1500	current regulation
pH-value		10.6	10.7	12.5	12.5	12.5	
Chromium	mg/l	< 0.002	< 0.002	0.030	0.075	0.100	
Vanadium	mg/l	0.028	0.004	0.050	0.100	0.250	
Fluoride	mg/l	< 0.4	< 0.4	0.75	2.0	2.0	
	Leaching column test w/s 2/1 (0/32 mm)			SWS-1	SWS-2	SWS-3	upcoming regulation
el. conductivity	µS/cm	113	177	10 000	10 000	10 000	
pH-value		10.0	10.4	9-13	9-13	9-13	
Chromium	mg/l	< 0.002	< 0.002	0.110	0.190	0.250	
Molybdenum	mg/l	0.013	0.011	0.055	0.400	1.000	
Vanadium	mg/l	0.085	0.170	0.180	0.450	1.000	
Fluoride	mg/l	< 0.4	< 0.4	1.1	4.7	8.5	

New application

In addition to the improvement in quality, also new markets like cement industry were investigated. In several field tests a similar treated slag was water granulated by a mobile equipment of the FEhS-Institute to produce a type of granulated slag from the EAF-slag with cementitious advantages, see Figure 4.



Figure 4: Water granulation of treated EAF slag by FEhS

For this purpose, a platform was erected in the area of the slag pit; on the platform, the mobile granulation device was put up and liquid slag was taken from the slag pot by a long spoon. Based on the results of these trials, there is evidence that a glassy phase with latent hydraulic properties can be produced in general. To test the cementitious properties, mortar prisms were produced in a 50:50 mixture with CEM I and compressive strengths were measured after 2, 7, 28 and 91 days. The results

show that BTI 20 has a bad performance with no market chances. BTI 28 is much better due to a higher glass content and therefore latent hydraulic properties. The compressive strengths are in the average of FEhS GBFS-monitoring, a GBFS database from all blast furnaces from Germany, the Netherlands and Austria. Nevertheless, there is still need for optimisation, due to the expensive treatment.

Conclusion

It was shown that a metallurgical treatment of EAF slag is possible from technical side of view. The main challenges are the logistics inside the steel work, incidence behaviour and economic aspects. Further investigations are necessary to develop a rugged process, an injection system for continuous operation and a crusher to handle the very dense and hard slag. The metal has a low P-content, but it's still too high to recycle it in EAF, so use in other metallurgical industries must be investigated.

Acknowledgement

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