

THE EFFECTIVENESS OF DEPHOSPHORIZATION WITH AND WITHOUT FLUORSPAR USING IN THE ELECTRIC ARC FURNACE STEELMAKING

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Abstract

This article deals with comparison of parameters from two different technologies – one with fluorspar and another one without fluorspar using. Fluorspar is being eliminated due to its toxicity and negative environmental impact. The statistical evaluation of 60 campaigns of electric arc furnace plant was performed. According to the graphical relationships and average values of parameters, it was found that chemical compositions of slags did not change practically and high effective dephosphorization can be achieved without fluorspar too. The negative influence of fluorspar using on the refractory lining and also negative influence of rising temperature on the phosphorus removal were confirmed.

Keywords: steels, slag, fluorspar, phosphorus, electric arc furnace.

1 Introduction

The modern basic oxidative steelmaking technologies such as oxygen converters (BOF) or electric arc furnaces (in further EAF) are inevitably associated with the dephosphorization process. During the evolution of these technologies, the productivity has been continuously increasing, whilst the tap-to-tap times, consumptions of fluxes and energy have been gradually decreasing. The intensification of competition pressure among the steel producers has led to the demands for maximally accepted phosphorus content in the steel products of about P max. 0.015 wt% (0.010 wt%), however high-quality charge materials (especially metallic scrap for EAF) are becoming scarce. The steelmakers are looking for the possibilities of sustainability or even improvement of dephosphorization in the more and more complicated conditions (shorter tap-to-tap times, lowering economical costs and consumption of materials). The attention is mainly attracted to the slags – how to accelerate the process of liquid slag forming, how to absorb as much phosphorus as possible, but simultaneously how not to exceed the rephosphorization point [1, 2].

Effective dephosphorization in the steelmaking processes (including EAF process) requires optimal content of iron oxides in the slag (ideally 20 - 35 wt%) [3, 4]. It also requires lower temperatures and higher values of slag basicity [2, 3]. The level of iron oxides (in further FeO) in the EAF slag is related to the scrap and charge quality, addition of oxidative fluxes, but above all it's linked with the parameters of oxygen blowing. The temperature is continuously rising throughout the heat. Due to danger of rephosphorization, it's very important not to exceed

neither the critical content of FeO nor the critical temperature [3]. In general, the high basicity level is provided by charging of lumpy metallurgical or dolomitic lime in the beginning of the heat. The common problem is a slow dissolution of conventional basic lumpy fluxes [5]. Better dissolution requires longer time or higher temperatures (this is undesirable due to danger of rephosphorization) or the dissolution process could be also improved by changes in technology such as modification of conventional fluxes or utilization of fluidizing agents. The injection of pulverized lime (separately or as a mix with other materials) directly into the melt volume seems to be the ideal option within the method of flux modification [6, 7, 8]. The phosphorus removal has been significantly enhanced by the utilization of fluidizers – the best known fluidizer is a fluorspar. The lumps of fluorspar added to the furnaces with the conventional fluxes were used world-wide [6, 7, 9]. Thanks to the presence of fluorspar (CaF_2) the melting temperature of the slag and slag viscosity were remarkably decreased and inversely dissolution rate of fluxes, slag evolution rate, slag foaminess, phosphate capacity were increased [10-14]. It was found that just 1 – 4 wt% of CaF_2 in EAF slag is enough to increase the slag phosphate capacity to a double or even triple values [15, 16]. According to [14], this phenomenon is elucidated as a decline of activity coefficient of P_2O_5 caused by CaF_2 addition. But in [17] it's claimed, that it's happening by the hindering of dicalcium silicate formation. Despite previous opinions, author of [18] is convinced that the distribution of P between slag and metal is not clearly affected by the CaF_2 presence and the effect of moderate additions of CaF_2 corresponds to the effect of the same quantity of lime. Fluorspar has no influence on the basicity. It doesn't participate in the dephosphorization process in a chemical way, but only physically, because within the substitution of lime by the same amount of fluorspar, the phosphate capacity is radically decreased [15, 16].

However, fluorides are released in the practical use of fluorspar and these compounds are very dangerous for human health (toxicity), environment (ecological threat) and are also harmful for furnaces (negative influence on the refractory lining [19]). Therefore the development of optimal basic fluorspar-free slags is unavoidable and urgent matter [10, 12]. Theoretically, fluorspar as a slag fluidizer can be replaced by colemanite ($2\text{CaO}\cdot 3\text{B}_2\text{O}_3$), manganese ore, ilmenite (FeTiO_3), crushed chamotte bricks, slags from manganese production, Al_2O_3 , Na_2O or BaO -based fluxes, chlorides, etc [5, 7, 12, 15, 20]. And yet, if the optimal chemical composition of the slag is achieved, the slag is then sufficiently fluid and has a high phosphate capacity so there's no need for any fluidizers [6, 18].

2 Materials and methodic

Based on the statistical treatment of EAF plant data, the parameters of slags and slag practices of two different technologies (with and without CaF_2 using) were compared. Thirty campaigns (~ 5700 heats) for each technology were evaluated. The technology was operated in a following manner: Some standard amount of lime was added to the furnace after each charging bucket. There was also added some smaller amount of fluorspar in the first case. The reduction (FeO) and foaming of the slag was provided by the injection of anthracite fines directly to the melt volume. The dephosphorization was quantitatively evaluated as a ratio of phosphorus contents in the slag and metal i.e. $\Phi_p = (\text{P}_2\text{O}_5)/[\text{P}]$. In this EAF plant, fluorspar was used during nearly the whole year 2005. The fluorspar charging was gradually limited to the end of year 2005 and during 2006 it was practically eliminated – it was used only in the seldom cases of crusty slags (1 heat of 100). Thus, practical consumption of CaF_2 in 2006 was close to 0 kg per ton of metal. The slag and metal samples were taken manually from the slag door area by EAF operator

approximately 7 – 12 minutes before EAF tapping for both technologies. The metal samples were analyzed using spectrometry, slag samples were analyzed by X-ray spectrometer. The temperature was measured by thermocouple several minutes before tapping.

3 Results and discussion

At first, the average values of parameters from each campaign (30 campaigns with fluorspar and 30 campaigns without fluorspar using) were evaluated. Then the average values of all of previous data were calculated (see **Table 1**), so a final comparison of technologies could be done.

Table 1 The comparison of average parameters for two different technologies

Average values of parameters		CaF ₂ addition	▲ Without CaF ₂
fluorspar	kg/t	1.02	0
metallurgical lime	kg/t	36.48	36.94
anthracite	kg/t	6.06	6.02
%CaO in slag	wt %	33.19	33.07
%Al ₂ O ₃ in slag	wt %	5.59	5.87
%SiO ₂ in slag	wt %	14.01	13.88
%MgO in slag	wt %	2.48	2.77
%MnO in slag	wt %	5.10	5.35
%FeO in slag	wt %	28.26	27.88
%Cr ₂ O ₃ in slag	wt %	1.24	1.16
%TiO ₂ in slag	wt %	0.47	0.40
%P ₂ O ₅ in slag	wt %	0.834	0.800
B ₂ = (%CaO)/(%SiO ₂)	-	2.38	2.41
Σ (%FeO + %MnO)	wt %	33.36	33.23
Σ of basic oxides	wt %	40.09	40.27
Σ of acidic oxides	wt %	26.55	26.50
[%P] in metal	wt %	0.008	0.007
Φ _p = (P ₂ O ₅)/[P]	-	103.23	109.36
Temperature	°C	1588.30	1590.80
Heats per campaign	-	186.50	193.33

When comparing the individual parameters in **Table 1** the following facts could be deduced: In the technology without CaF₂ using, contrary to that with CaF₂ charging, the economical savings were acquired (thanks to elimination of fluorspar) although the lime consumption was increased (+ 0.46 kg/t). The consumption of fine anthracite (slag foaming agent) was changed negligibly (saving of about 0.04 kg/t). According to the comparison of average slag parameters (contents of individual chemical components of the EAF slag or their sums) it's clear that the elimination of CaF₂ practically didn't affect the slag chemistry. This fact is in accordance with negligible change in basicity ratios and above all, since there were minimal differences between average (P₂O₅) and [P] contents, it's logical that the Φ_p values were very similar. Thus, it's possible to say that the phosphorus removal has nearly the same effectiveness, it was even better in the case without CaF₂ (Φ_p difference + 6.13 in the case without CaF₂), see **Table 1**. **Fig.1** illustrates the relationships of Φ_p vs. fluxes consumption for both technologies. According to curves in **Fig.1**, it is showed that dephosphorization wasn't affected by change in flux practice. Phosphorus removal is strongly related to temperature – it's well-known that increase in temperature has

detrimental consequences (rephosphorization). Within two technologies, as can be seen in **Table 1**, the average temperature was higher (+ 2.5 °C) in the case without CaF₂.

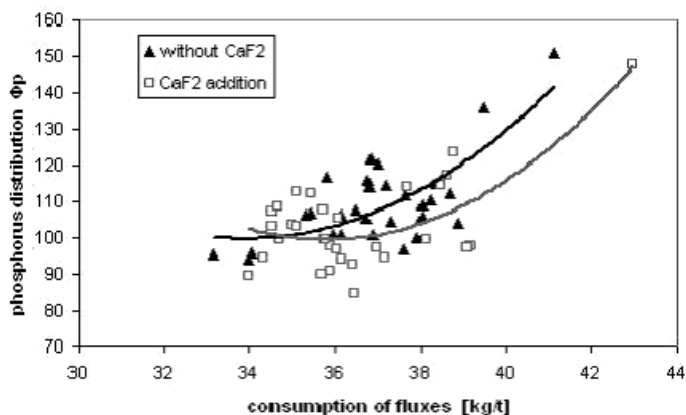


Fig.1 Phosphorus distribution Φ_p as a function of consumption of fluxes for 2 different technologies

Fig.2 represents the relationships of Φ_p vs. sampling temperature for both technologies. Φ_p values are decreasing with rising temperature. It's in accordance with theory (negative effect of rising temperature [3]). According to curves in **Fig.2**, it could be concluded that with increase in temperature the dephosphorization efficiency was even better in the case of technology without CaF₂, but the fact of influence of higher scatter must be underlined. Nowadays, it's known that fluorspar practice has negative effect on the lifetime of refractory lining. The comparison of data from **Table 1** proved that the lifetime of EAF hearth lining was higher (+ 6.83 heats/campaign) in the case of technology without CaF₂.

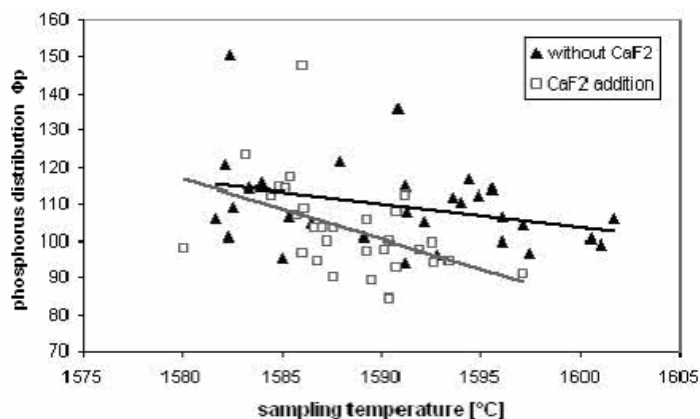


Fig.2 Phosphorus distribution as a function of sampling temperature for 2 different technologies

4 Conclusions

The aim of presented article was to compare the dephosphorization effectiveness in the electric arc furnace for different technologies - with and without fluorspar using. In the steelmaking, fluorspar as slag fluidizer has been eliminated due to safety, ecological and technological reasons. It's replaced by other fluidizers or there is an effort of achieving the optimal slag

fluidity without any fluidizers. In this study, a set of 60 campaigns from EAF plant was analyzed. Based on the comparison of average data for each technology, it's possible to say that the elimination of CaF_2 from the EAF process didn't affect the technology in a negative point of view. Practically, there weren't registered any significant changes in average compositions of EAF slag or in slag basicities. The technology without CaF_2 had lower total consumption of fluxes and anthracite and longer lifetimes of hearth refractory lining. The negative influence of rising temperature on Φ_p values was seen in both cases. Despite of relatively higher average temperature and lower fluxes consumption the technology without CaF_2 had a similar or even higher Φ_p values as older technology. It can be concluded that the fluorspar-free flux practice has the similar or even better dephosphorizing efficiency as the older practice. The negative factors that could scatter the results must be mentioned: manual sampling, possible contamination of samples, oxygen jet using before sampling, vicinity of oxy-fuel burner and especially human factor.

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