CHEMICAL ENGINEERING TRANSACTIONS

VOL. 61, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar S Varbanov, Rongxin Su, Hon Loong Lam, Xia Liu, Jiří J Klemeš

ISBN 978-88-95608-51-8; **ISSN** 2283-9216

DOI: 10.3303/CET1761086

Assessment of Treatment Configurations through Process Simulations to Improve Basic Oxygen Furnace Slag Reuse

Ismael Matino[a],*, Teresa Annunziata Branca[a], Valentina Colla[a], Barbara Fornai[a], Lea Romaniello[b]

[a]Scuola Superiore Sant'Anna, TeCIP Institute – ICT-COISP, via Moruzzi 1, 56124 Pisa, Italy
[b]ILVA S.p.A. Taranto Works, SS Appia Km 648, 74123 Taranto, Italy
i.matino@sssup.it

The European steel sector aims at improving its material efficiency by increasing the by-products recycling rate. This can lead to approach the ambitious "zero-waste" goal, by minimising the need for landfilling, saving raw materials, reducing emissions and contributing to improve the economic sustainability of the production cycle. The steelmaking process produce several by-products: slags are the main one and can be used to make different products, including cement, fertilisers and asphalt. This paper presents a work aiming at obtaining reusable fractions from the Basic Oxygen Furnace slag. Two Aspen Plus®-based models were developed and exploited: a model of the slag treatments to make sensitivity analyses, providing information about different slag treatment configurations, particularly on different magnetic separation solutions, and a model computing the pellet composition according to the different inputs. Other models, developed through reMIND® software, are material flow superstructures that implemented results from the treatment model. They allowed assessing the best route for internal or external reuse of the slag fraction, taking into account process, environmental and economic impacts and making optimization assessment. They are able to identify the slag quality that is more suitable for the reuse. The developed models can provide significant improvements based on economic and environmental sustainability (e.g. increase of by-products recycling, reduction of slag recovering in the internal quarry, reduction of treatment costs, etc.) compared to the current use at ILVA Steelworks.

1. Introduction

The European steel industry is committed to increase the recycling rate of by-products produced in steelmaking processes, such as discussed in (Peters et. al. 2015), also according to the ever more stringent European regulations. Significant environmental and economic benefits are expected, such as prevention of waste landfilling, reduction of CO_2 emissions and natural resources exploitation. The main by-products of the steel sector are slags, dusts, mill scales and sludges. Slags represent the 90 % by mass (World Steel Association, 2017) of the total produced by-products. Basic Oxygen Furnace (BOF) slag is a by-product of the integrated steelmaking, resulting from dolomite and other fluxes addition in the furnace during the conversion process of the pig iron into steel. For the Italian legislation BOF slag is considered as a non-hazardous waste, which can be recovered in a quarry, according to legislation limits of leaching tests. The BOF slag composition includes CaO, SiO_2, Al_2O_3, Fe_xO_y, MnO, P_2O_5 and VO_x, depending on raw materials qualities and produced steel grades. Over the last few years, the slag produced in the BOF decreased thanks to new techniques. However, further efforts must be applied to achieve even better results, in order to approach the "zero-waste" target and to improve resources savings.

In order to increase the recycling rate of slags, their composition must be clearly identified and carefully considered, so as avoid any negative effects on the environment (Dippenaar, 2005). Investigations on the slag characterization and on possible slag pre-treatments have recently carried out (Matino et al., 2015). On this subject, the optimization of the slag products and the identification of suitable downstream ad-hoc recovery treatments can increase the recycling of slag.

Please cite this article as: Matino I., Branca T.A., Colla V., Fornai B., Romaniello L., 2017, Assessment of treatment configurations through process simulations to improve basic oxygen furnace slag reuse, Chemical Engineering Transactions, 61, 529-534 DOI:10.3303/CET1761086

In order to obtain a Fe-richer product, which is suitable for the sintering process, slag, after discharging into the slag yard, is cooled and subject to magnetic separation and iron recovering (Horii et al., 2012). The slow cooling application to the BOF slag can produce a fraction with high iron and low phosphorus content (Wang et al., 2012). The cooling conditions are important for mineral formation and crystallization. In particular, slow cooling promotes the good distribution of crystals into the slag (Wang et al., 2012). After magnetic separation, BOF slag can be internally recovered as raw material or used in different field of applications (World Steel Association, 2010), such as in overlays, bearing layers in mixed concrete, according to (European Regulation 305/2011), road foundations and in concrete mixtures cement production and restoration of marine environments (Zhang et al., 2011), according to the national legislation. It can be also reused in ironmaking and steelmaking processes as raw material (thanks to the high content of valuable elements like iron). The not magnetic fraction can be used for soil fertilization or amendment considering the good results in terms of crop yields and quality obtained after long-term field or lysimeter trials (Branca et al., 2014) and the negligible effects in terms of groundwater pollution (Morillon et al., 2015); while the magnetic fraction can be employed in pellets production (Kawatra et al., 2002). It has been shown that the application of wet magnetic separation helps to obtain low impurities in the fraction. By coupling the weak magnetic separation with the selective size screening, the recycling rate of slag can be improved (Ma and Houser, 2014). On the other hand, the application of a strong magnetic field can allow to separate Fe_tO matrix in the crushed BOF slag (Yokoyama et al., 2007), by allowing the recovered slag of higher quality, which can be further improved by repeating the separation practice (Kubo et al., 2010). Previous studies underlined the slag enrichment through magnetic separation and the consequent effects on the sinter quality (Bölükbaşı and Tufan, 2014).

As technical, economic and environmental aspects can affect the recycling rate, the use of process models and simulations can help to investigate them in order to assess processes improving material and energy efficiency, which can improve the environmental and economic sustainability in the steel sector, such as discussed in (Matino et al., 2015a). In this regard, some recent studies have been carried out. For instance, as steelmaking plants are huge energy consumers, energy efficiency can be significantly improved by applying the total site approach using a "Total Site Profile (TSP) analysis", based on pinch technology (Matsuda et al., 2012). Modeling of different sub-plants in an integrated steelworks allowed the calculation of mass and energy balances in different scenarios of operation in order to optimize the process gas network (Porzio et al., 2014). A recent study, focused on improving the sustainability of electric steelworks, exploited a simulation model developed by Aspen Plus® in order to investigate the correlations among electric energy consumption, steel grade, slag quantity and composition (Matino et al., 2016a).

Process simulation is also the topic of the present work, which was carried out within the European project, entitled ''Removal of Phosphorus from BOF slag'' (PSP-BOF). The work aimed at optimizing by-products reuse scenarios at ILVA Steelworks in Taranto (Italy), with a particular focus on BOF slag reuse. As this by-product is currently recovered in internal quarry, in order to increase its internal recycling through the pellets production, some process models were developed. Several information were used: experimental information, the achieved results on the evaluation through Aspen Plus®-based model of pre-treatments of other by-products (Colla et al., 2015), that are potentially reusable in pellet production together with BOF slag or can be directly reused and the preliminary results obtained for BOF slag with empirical MS Excel® – based model (Matino et al., 2015b). The developed models aimed at considering slag treatment and processing as well as production of internal reusable products. Two Aspen Plus®-based models are proposed: a model for different BOF slag treatment configurations, taking into account different solutions for magnetic separation and a model computing pellet composition, which takes into account different inputs. Models developed by reMIND® software, whose features are described in (reMIND tremind) and in (Karlsoon, 2011), consist in material flow superstructures that implement the results achieved in the treatment models, in order to assess the route which mostly allows the reuse of by-products (especially BOF-slag) and gets a high-quality secondary raw material (e.g. pellets to feed sinter plant). The work developed by Matino et al. (2016b) was improved and deepened. Process, environmental and economic impacts are considered during the optimization assessment. Moreover, the models allowed comparing the novel analysed applications to the current use of by-products at ILVA Steelworks.

The paper is organized as follows: Section 2 presents the modeling phase; in Section 3 the achieved results are discussed, while Section 4 includes some concluding remarks.

2. Materials and Methods

In order to assess BOF slag treatments, processing and production of reusable products as well as to identify the best route for by-products internal or external reuse, two models based on the commercial software Aspen Plus® V. 8.6 and two models developed by means of the reMIND® software were developed. The first ones are flowsheet-based while the second ones are flow superstructures and they are linked as depicted in Figure 1A. One of the two Aspen Plus® models is a "scenario data generator", which allows considering and assessing different process configurations and different BOF slag types, while the other one provides the composition of one of the possible secondary products, i.e. the pellets, after that the mixture for their production was optimized. The two reMIND models are mass flow superstructures: the former one identifies the best route for reusing BOF slag (and other by-products), while the latter one points out the best BOF slag quality to be reused. The models were setup and tuned starting from laboratory tests and industrial data collected during the project, especially at ILVA. Moreover, also results of a previous project named REFFIPLANT (Matino et al., 2016b) funded by the Research Fund for Coal and Steel were used. For instance, Particle Size Distributions (PSD), distribution of slag component according to cooling procedure, BOF slag fraction compositions, separation efficiencies, etc, were exploited.

The first Aspen Plus® model considers the main slag treatments and processing steps, such as cooling, grinding and sieving, and magnetic separation. Some stream duplicator blocks included in the model allow the simultaneous assessment of different treatment configurations or process units. The model computes the following parameters:

- distributions of chemical compounds;
- PSD after grinding;
- composition of the main sieved fractions (e.g. ≤ 2mm and > 2mm);
- compositions of magnetic and non-magnetic fractions after different magnetic separations (manual magnetic separation with neodymium magnet, Wet High Intensity– WHI - magnetic separation with Davis Tube at 1.2T, Wet Low Intensity - WLI - magnetic separation with low intensity wet drum separator and a magnetic field strength less than 1.2T, dry magnetic separation with rotatory separation drum having a neodymium magnet and a magnetic field intensity of about 0.2 T at the surface);
- approximate estimation of required energy in the grinding step based on Bond's Law.

The model was tuned by exploiting the experimental results related to a selected BOF slag from ILVA Steelworks. The comparison between results of the tuned model and results of the real case showed insignificant errors. For instance, Figure 1B shows that the real and simulated slag fractions compositions after grinding and sieving are very similar, and the same behaviour is observed also for other monitored parameters. The results of the Aspen Plus® model were used to point out which was the best slag treatment route, by taking into account the composition of the fractions resulting from treatment and by exploiting them for further economic and environmental constraints. To this aim, two reMIND-based superstructures mass models were developed, upgrading the reMIND superstructure developed within the REFFIPLANT project to optimise the reuse of different by-products/wastes (Matino et al., 2016b). The first superstructure included the different magnetic separations of BOF slags and the different fates of the BOF sludge and mill scales that were considered as potentially suitable for pellets production. Each treatment was characterized by some normalized indicators connected to the following parameters: final product qualities (depending on the iron or phosphorous content. It is defined as the ratio between the minimum quality value and the quality related to the considered treatment and for this reason lower its value, higher the quality), environmental impact, treatment costs, revenues (lower this indicator, higher the revenues), efficiency of separation (lower this indicator, higher the efficiency). These indicators constitute the objective functions considered in the optimization. A second more simplified reMIND-superstructure was developed to identify the best BOF slag to be reused. This was done through another multi-objective optimization by minimizing all the objective functions that were considered in the analysis previously performed.

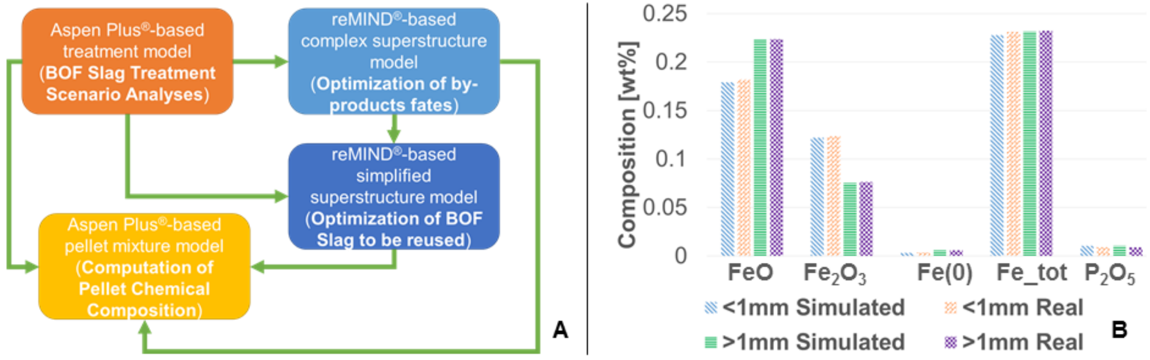

Figure 1: A. Links between the Developed Models; B. Comparison between real and simulated composition of slag fractions after grinding and sieving.

3. Results and Discussions

In order to reduce the amount of BOF slag recovered in internal quarry and to increase the recycling of by-products, the production of pellets was analysed: BOF slag, BOF sludge and mill scale were considered, to the aim of increasing the BOF slag reuse, as BOF sludge and mill scale are already used in the sintering process.
The final fractions of the three BOF slag (A, B and C), both magnetic and non-magnetic, were obtained after treatments, such as slow cooling, grinding and sieving, magnetic separation for fraction with a PSD <= 2mm and > 2mm, mixing of magnetic fraction and mixing of non-magnetic fraction. The treatment model provides these results considering different magnetic separation techniques and extending the outcomes of real experimentation. Table 1 and Table 2 show results as portion of magnetic and non-magnetic fractions and of obtained compositions.

Table 1: Magnetic fractions and their compositions after different separation solutions and with different BOF slags.

	Magnetic Fractions											
	Manual			WHI			WLI			Dry		
	A	B	C	A	B	C	A	B	C	A	B	C
	wt %											
CaO	30.1	35.9	29.4	37.4	42.9	36.4	30.8	36.7	30.2	42.9	50	41.9
SiO_2	7.9	8.5	8.8	11	11.4	12.2	7.9	8.4	8.7	12	12.3	13.2
Al_2O_3	2.1	2.2	2.3	1.8	1.9	2.0	1.8	2.1	2.2	2.1	2.1	2.3
P_2O_5	0.6	1.1	0.7	0.9	1.5	1	0.6	1.1	0.7	1.0	1.6	1.2
Fe(0)	0.6	0.5	0.6	0.7	0.6	0.7	0.4	0.3	0.4	0.7	0.5	0.7
FeO	25.9	20.6	25.6	16.6	12.7	16.3	25.5	20.2	25.2	15.8	12	15.6
Fe_2O_3	18.4	14.6	18.2	17.2	13.1	16.9	18.1	14.3	17.9	16.3	12.4	16.1
Other	14.4	16.6	14.4	14.4	15.9	14.5	14.9	16.9	14.7	9.2	9.1	9
Magnetic Fraction	27	26	27	41	40	41	21	20	21	36	35	36

Table 2: Non-Magnetic fractions and their compositions after different separation solutions and with different BOF slags.

Non-Magnetic Fractions												
	Manual			WHI			WLI			Dry		
	A	B	C	A	B	C	A	B	C	A	B	C
	wt %											
CaO	47.5	52.6	46.0	46.5	52.0	45.1	45.9	51.2	44.5	42.7	47.9	41.3
SiO_2	14.4	14.3	15.7	13.7	13.8	15.0	13.9	13.9	15.2	13.0	13.1	14.2
Al_2O_3	2.1	2.1	2.3	2.3	2.3	2.5	2.1	2.1	2.3	2.1	2.1	2.3
P_2O_5	1.2	1.9	1.3	1.1	1.8	1.3	1.1	1.8	1.3	1.0	1.7	1.2
Fe(0)	0.3	0.2	0.3	0.1	0.1	0.1	0.4	0.3	0.4	0.2	0.1	0.2
FeO	16.4	12.1	16	20.6	15.3	20.2	17.2	12.8	16.9	20.7	15.5	20.2
Fe_2O_3	8.3	6.1	8.1	6.8	5.0	6.6	9.2	6.8	9.0	8.1	6.1	7.9
Other	9.8	10.7	10.3	8.9	9.7	9.2	10.2	11.1	10.4	12.2	13.5	12.7
Non-Magnetic Fraction	73	74	73	59	60	59	79	80	79	64	65	64

The results show that WHI magnetic separation leads to separate a bigger magnetic fraction, but with iron compounds less concentrated compared to the magnetic fraction after Manual and WLI magnetic separations. This was due to the bigger entrainment of non-magnetic fraction by the WHI magnetic separation; nevertheless, in absolute terms the recovered iron fraction with WHI is bigger than with the other magnetic separation techniques. On the other hand, the kind of magnetic separation poorly affects the iron and phosphorous compounds content in the non-magnetic fractions. Moreover, slag A provides fractions containing higher amount of iron compounds, while slag B provides fractions with higher amount of P_2O_5.
In order to achieve the best route for reusing BOF slag, BOF sludge and mill scale, the reMIND-based superstructures were exploited. Different multi-objective optimizations scenarios were assessed, in order to minimise different combination of previously defined indicators, such as Environmental Impact (OP1), Quality + Environmental Impact (OP2), Costs and Revenues + Environmental Impact (OP3), the minimization of each

indicators (Global Optimization – GOP). Table 3 shows the list of results as by-products/wastes percentage distribution.

Table 3: Results of reMIND best route-optimization

	Agglomeration			Pelletization			Fertiliser and Other Use			Disposal or Environmental Recovery		
	wt %											
	OP1	OP2	OP3 & GOP	OP1	OP2	OP3 & GOP	OP1	OP2	OP3 & GOP	OP1	OP2	OP3 & GOP
BOF Slag	N.a.	N.a.	N.a.	20.4 (WLI)	26.4 (M)	40.9 (WHI)	79.6 (WLI)	73.6 (M)	59.1 (WHI)	0	0	0
BOF Sludge	0	0	0	100	100	100	N.a.	N.a.	N.a.	0	0	0
Mill Scale	0	100	100	100	0	0	N.a.	N.a.	N.a.	N.a.	N.a.	N.a.

Results achieved through the optimization could allow not only reducing the disposal of by-products but also increasing their reuse in different identified routes. Moreover, the best solution consists in using the BOF slag B and a little fraction of slag C. This provides relevant iron content in the pellets as well as higher P_2O_5 content in the non-magnetic fraction, which makes it suitable to be used for the production of fertilisers. This result comes from the second reMIND model which gives the optimized pellet mixture in the case of GOP: magnetic fraction of BOF slag obtained through WHI (57 wt%: B – 99 wt% and C – 1 wt%), BOF sludge (35 wt%), lime (1 wt%), cement (7 wt%).

Finally, a simulation aimed at finding the chemical composition of optimized pellet mixture was carried out through the other Aspen Plus®-based model and by taking into account each simulated results and some experiments carried out during PSP-BOF project. This last model is able to mix the magnetic fractions of the three BOF slags, obtained with the treatment model, BOF sludge, mill scale, cement and lime. The data can be passed from one Aspen Plus-based model to the other one as they are connected to an Excel-sheet through the Aspen Simulation Workbook® and the two Excel sheets are linked together. This feature allows also an easy model management. Table 4 shows the resulting pellet chemical composition.

Table 4: Resulting pellet chemical composition.

Component	Fe_tot	P_2O_5	CaO	SiO_2	MgO	Al_2O_3	MnO_2	C	Other
wt%	34.38	0.89	32.08	8.65	7.90	1.66	2.42	2.80	9.22

4. Conclusions

The models described in the present paper aimed at obtaining the best solutions to treat BOF slag, the best slag to be reused, the best reusing route and the obtained pellets composition. Although the achieved data need further analyses and tests, the developed models show some innovative aspects. The joint application of the two software solutions can be considered a useful tool to be exploited by industrial staff in order to analyse possible scenarios on the BOF slag use. This can lead to improvement of the internal reuse for pellets production by saving time and natural resources. Future work aimed at the implementation of the internal reuse of pellets production will consist in the assessment of the economic viability of the proposed solutions.

Acknowledgments

The work described in the paper was developed within the project entitled ‘‘Removal of Phosphorus from BOF slag’’ (PSP-BOF) (RFSR-CT-2013-00032) that have received funding from the Research Fund for Coal and Steel of the European Union. The sole responsibility of the issues treated in the paper lies with the authors; the Commission is not responsible for any use that may be made of the information contained therein.

References

Bölükbaşı Ö., Tufan B., 2014, Steelmaking slag beneficiation by magnetic separator and impacts on sinter quality, Sci. Sinter, 46, 331–344.

Branca, T.A., Pistocchi, C., Colla, V., Ragaglini, G., Amato, A., Tozzini, C., Mudersbach, D., Morillon, A., Rex, M., Romaniello, L., 2014, Investigation of (BOF) Converter slag use for agriculture in europe, Metallurgical Research and Technology, 111 (3), 155-167.

Colla V., Matino I., Alcamisi E., Porzio G.F., Romaniello L. Rosito F., 2015, By-products recycling in iron & steel plant: comparison between oily millscale treatments. METEC & 2nd ESTAD 2015, Düsseldorf, Germany.

Dippenaar, R., 2005, Industrial uses of slag (the use and re-use of iron and steelmaking slags), Ironmaking & Steelmaking, 32, 35–46.

European Regulation 305/2011 of the European Parliament and of the Council of 9 March 2011 laying down harmonised conditions for the marketing of construction products and repealing Council Directive 89/106, EEC, Brussels, Bwelgium.

Horii K., Tsutsumi N., Kitano Y., Kato T., 2012, Processing and reusing technologies for steelmaking slag. Shinnittetsu Giho. 394, 125–131.

Karlsson, M., 2011, The MIND method: a decision support for optimization of industrial energy systems—principles and case studies, Applied Energy, 88(3), 577–589.

Kawatra S.K., Ripke S.J, 2002, Pelletizing steel mill desulfurization slag, International journal of mineral processing, 65, 165-175.

Kubo H., Matsubae-Yokoyama K., Nagasaka T., 2010, Magnetic separation of phosphorus enriched phases from multiphase dephosphorization slags, ISIJ International 50(1), 59–64.

Ma N., Houser J.B., 2014, Recycling of steelmaking slag fines by weak magnetic separation coupled with selective particle size screening, Journal of Cleaner Production, 82, 221-231.

Matino, I., Colla, V., Romaniello, L., Rosito, F., Portulano, L., 2015a, Simulation techniques for an Efficient Use of Resources: An overview for the steelmaking field, 2015 World Congress on Sustainable Technologies, WCST 2015, London, UK, 48–54.

Matino I., Branca T. A., Alcamisi E., Colla V., Romaniello L., 2015b, Evaluation of a BOF slag recovery treatment combining experimental and simulation studies, 3rd International Conference on Sustainable Solid Waste Management TINOS 2015, Tinos Island (Greece), July 2–4.

Matino I., Colla V., Colucci V., Lamia P., Baragiola S., Di Cecca C., 2016a, Improving Sustainability of Electric Steelworks through Process Simulations, Chemical Engineering Transactions, 52, 763-768 doi:10.3303/CET1652128.

Matino I., Colla V., Branca T.A., Romaniello L., 2016b, Optimization of By-Products Reuse in the Steel Industry: Valorization of Secondary Resources with a Particular Attention on Their Pelletization, Waste and Biomass Valorization, 1-13, doi: 10.1007/s12649-016-9768-x.

Matsuda K., Tanaka S., Endou M., Iiyoshi T., 2012, Energy saving study on a large steel plant by total site based pinch technology, Applied Thermal Engineering, 43, 14-19.

Morillon A., Mudersbach D., Rex M., Spiegel H., Mauhart M., Tuomikoski S., Branca T.A., Ragaglini G., Colla V., Romaniello L., 2015, Impact of long-term application of blast furnace and steel slags as liming materials on soil fertility and crop yields, 8th European Slag Conference EUROSLAG 2015, Linz (Austria) October 21–23.

Peters, K., Malfa, E., Colla, V., Brimacombe, L., 2015, Resource efficiency in the Strategic Research Agenda of the European Steel Technology Platform, 2015 World Congress on Sustainable Technologies, WCST 2015, London, UK ,34–39.

Porzio G. F., Colla V., Matarese N., Nastasi G., Branca T. A., Amato A., Fornai B., Vannucci M., Bergamasco M., 2014, Process integration in energy and carbon intensive industries: An example of exploitation of optimization techniques and decision support, Applied Thermal Engineering 70, 1148-1155.

reMIND tremind, MILP modelling of your industrial system of choice. <code.google.com/archive/p/tremind/>, accessed 01.01.2017.

Wang D., Jiang M., Liu C., Min Y., Cui Y., Liu J., Zhang Y., 2012, Enrichment of Fe-containing phases and recovery of iron and its oxides by magnetic separation from BOF slags, Steel Research International, 83, 189–196.

World Steel Association, 2010, Steel industry by-products - Project group report 2007–2009, Brussels, Belgium.

World Steel Association, 2017, <www.worldsteel.org> accessed 18.04.2017.

Yokoyama K., Kubo H., Mori K., Okada H., Takeuchi S., Nagasaka T., 2007, Separation and recovery of phosphorus from steelmaking slags with the aid of a strong magnetic field, ISIJ International, 47(10), 1541–1548.

Zhang Y., Zhao F., Wang Y.G., 2011, Effects of influencing factors on distribution behaviours of vanadium between hot metal and $FeO\text{-}SiO_2$–(-TiO_2) Slag System, Steel Research International, 82(8), 940-950.