DEVELOPMENT OF INNOVATIVE SOLUTIONS FOR RECOVERY OF IRON FROM STEELMAKING SLAGS

Anna Semykina & Volodymyr Shatokha
National Metallurgical Academy of UkraineUkraine

Seshadri, Seetharaman
Royal Institute of Technology, Sweden

ABSTRACT

In the modern context, sustainable development strategy determines shifting of a focus in the domain of industrial wastes from general completeness of utilising/recycling to development of specific measures necessary to recover particular elements or compounds from the wastes in the most efficient way. A specific problem with Ukrainian steelmaking practice is the high content of iron oxide in the slags, upto 30% in some cases. These slags are unsuitable as construction materials or road fillings as iron oxide has detrimental properties "vis-a-vis" these applications. It is essential to remove iron oxide from the slag without serious cost-intensive metallurgical operation. Metal values in metallurgical slags are bound in the silicate matrix. A critical examination of the thermodynamics of slags reveals that the iron oxide in the silicate can be oxidized, by the choice of temperature and oxygen partial pressure (preferably air) to magnetite which can be magnetically separated. In the present work, oxidation of the iron values in slags to higher oxides was studied in laboratory scale. Synthetic as well as industrial slags were used in these experiments. The results demonstrate the feasibility of the method in the recovery of iron values from the slags.

INTRODUCTION

On a global perspective, during the production of iron and steel, large amounts of industrial waste or by-products accumulate every year. Recycling of these materials is of increasing interest worldwide. The major waste product of the steelmaking industry is slag. Millions of tons of slag are produced during operation of metallurgical plants around the world. The main constituents of these slags are CaO, SiO_2, Al_2O_3, MgO, FeO and Fe_2O_3.

The main field of application for steelmaking slags is civil engineering, especially road and waterway construction [1]. The steelmaking slag has not yet been utilized effectively. A significant amount of these slags remain in slag dumps, damaging the environment. This is well-illustrated in Figure 1. These solid wastes require many square kilometres of land for storage. In spite of significant efforts to decrease their harmful effects on the environment, there is no way to prevent contamination of soil and underground water.

Figure 1: Stockpiles of steelmaking slags of Ukrainian integrated plant JSC DMZ named after Petrovskiy

Steelmaking Slags in Ukraine

In the modern context, sustainable development strategy in the domain of wastes utilization determines shifting a focus from general completeness of recycling to specific attention to utilise elements containing the wastes in the most efficient way. This is well-illustrated in the context of steelmaking slags, with special reference to Ukrainian steelmaking practice. In Ukraine, under conditions when pig iron with relatively high silicon content (0.9% as average) is used as main component for steelmaking, the slag yield is as high as 100-110 kg/t [2]. With current volume of steelmaking capacities, it equals to 3.9-4.1 million tons of steelmaking slag per year to be utilized. The slag contains 44-56% of CaO and 15-33% of FeO and thus, is a very valuable material. For example, the yearly volume of the steelmaking slag contains up to 1 million ton of iron only in the form of oxides (non-magnetic part) and up to 2 million tons of lime. These volumes correspond to around 5 million tons of medium grade iron ore and 4 million tons of limestone which are non-renewable natural resources. Excavation, enrichment and processing of these materials are connected with significant consumption of energy, application of work force and pollution of the environment. Taking into account hundreds of millions tons of slags stored during the last 70-80 years of industrial era in Ukraine, it is evident that development of the most efficient solutions for utilizing steelmaking slag components is extremely important and is an urgent need for this country with short history of independence which is eager to make a breakthrough from past out-dated technologies to new cutting-edge engineering solutions. Conventional approach for the utilization of steelmaking slags is the removal of iron in metallic form existing in the slag by magnetic separation [3]. The non-magnetic part of the slag is mainly utilized directly as blast furnace burden, or as a component for sintering blend. But the slag contains also up to 12-17% of SiO_2 which is unwanted compound for ironmaking as it would lead to an increase of slag yield and coke consumption. Thus, this conventional scheme does not solve the problem of efficient slag utilization. It does not also match the principle of Sustainable Development Strategy and, in fact, even increases the volume of wastes produced in allied industries (ironmaking and cokemaking). Alternative solutions such as utilizing of the slag for production of cement are limited due to the high FeO content. Its application as the material for road construction is limited by the tendency to rapid disintegration [4, 5]. While methods to prevent such disintegration are developed, the iron values remain in the slag in the form of unrecovered oxides.

Concepts of Iron Recovery from Slags Oxides

Conventional approach to the recovery of iron from oxides envisages its reduction using carbon-based reductants [6]. This would increase the energy needs of the process and require suitable reductants. For example, carbon could be a natural choice as a reductant. Corresponding chemical reaction not only requires solid fuels but also produces gas with strong greenhouse effect :

$$2FeO(slag) + C = 2Fe(solid\ or\ liq.) + CO_2\ (gas) \qquad (1)$$

Important direction today is not only processing of steelmaking slag, but also extraction of metal values from newly produced slags as well as from the dumps.

A *green* approach to utilizing the steelmaking slag components applied in current research, is to transform iron from non-magnetic to magnetic form with the application of carefully tailored physicochemical process steps. This will allow further separation of iron from concomitant oxides and enable a selective recycling/utilization of iron-bearing and non-iron-bearing parts of the slag for specific purposes. From the technological point of view, pre-treated slag will be separated using magnetic method and iron oxides transformed to magnetic form will be removed for further utilization. The rest of the slag (non-magnetic) will be effectively used in production of cement binder or in other applications. Magnetic product may be utilized as the component for sintering blend or burden for pelletizing of iron ore.

The aim of the present work is to find a new, more ecologically clean and feasible method for the utilization of useful elements from the slags of metallurgical production (ferrous materials and non-ferrous materials).

The gas/slag reaction studies were used towards the objective of utilization of steelmaking slags by oxidation. The experiments were carried out in different oxidizing atmospheres in the temperature range 1623K-1823 K.

The TGA measurements, which monitor the weight changes and thereby the reactivity, were carried out with air as the oxidizing gas medium as well as with mixtures of air and carbon dioxide. The analysis of reaction products was carried out mainly by X-ray diffraction.

METHODOLOGY

Prior to the design of the experiments, thermodynamic calculations were carried out, with a view to establish the feasibility of the oxidation route towards iron recovery from slags as magnetite. Essentially, these preliminary calculations were intended to see the relative effects of air as well as CO_2 as oxidizing media so that the experiments could be suitably tailored with respect to temperature and oxygen partial pressure.

Five types of industrial slags as well as synthetic slags (binary system $FeO-SiO_2$ and ternary system $FeO-CaO-SiO_2$) were chosen for experiments (Table 1).

The basicities of the synthetic slags were chosen as 0.6, 0.8, 1.0 so that, for the given FeO content in the sample, the liquidus temperature of the designed slag is below the maximum temperature limit of the furnace, *viz* 1873 K.

Materials

The materials used in this investigation are: iron powder < 10 micron, with a purity of 99.9+% (metals basis); Fe_2O_3 powder < 5 micron, with a purity of 99+% ; SiO_2 powder with a purity of 99.5% ; CaO powder with a purity 99.9%; iron crucible with purity 99.9% metal basis; platinum foil with 0.1 mm (0.004in) thick, 99.99% (metals basis); hydrofluoric acid (HF). All these were supplied by E-merck, Darmstadt, Germany. The gases used in the experiments, Carbon dioxide, argon and air, were supplied by *Air Liquide*, Stockholm. *FeO* was prepared by mixing Fe and Fe_2O_3 in equimolar ratio and sintering the mixture at 1373 K in a vertical furnace in flowing argon after encapsulating the same in the iron crucibles. The 5 Ukrainian industrial slags used in the present work were obtained from the Ukrainian integrated plant JSC DMZ named after Petrovskiy. The complete chemical assay of these samples were obtained by X-ray fluorescence spectroscopy (Table 1).

Table 1: Chemical compositions of synthetics and industrial slags

No.	Composition, %								
	CaO	FeO	SiO_2	MgO	MnO	Cr_2O_3	Al_2O_3	P_2O_5	S
1	$2FeOSiO_2$								
2	40	20	40						
3	33	15	52						
4	26.25	30	43.75						
5	30	20	50						
6	44.52	21.91	15.56	6.64	3.65	0.2	0.753	0.79	0.062
7	47.26	22.79	12.35	5.18	4.38	0.2	0.756	0.939	0.212
8	50.18	22.94	10.44	4.06	3.78	0.2	0.596	0.92	0.198
9	44.08	17.44	16.46	8.47	4.77	0.2	0.832	0.966	0.082
10	30.26	34.15	12.33	4.18	5.74	0.2	0.51	0.752	0.11

Platinum crucibles for holding the slags were made from platinum sheets of 0.4 mm thickness. Synthetic slags were made from CaO, FeO, SiO_2 powders. All the reagents were mixed in required proportions in an agate mortar. SiO_2 powder was dried for 24 hours in a muffle furnace at 800ºC. CaO powder was dried at 1273 K in vertical furnace for 2 hours. Total mass of sample was 2 g. The powder mixtures were pressed into tablets under a total pressure of 5 tones.

Experimental

Experiments with Synthetic Slag in the Horizontal Furnace

An alumina reaction tube, (60 mm o.d. and 50 mm i.d.) was positioned in a horizontal resistance furnace equipped with KANTHAL SUPER 1800 heating elements with a maximum working temperature of 1973 K (Figure 2). The platinum crucibles with slag samples were placed in an alumina holder that had a provision for four platinum units. This holder was placed in the even-temperature zone of the furnace. The sample temperature in the furnace was monitored by a calibrated Pt-30 pct Rh/Pt-6 pct Rh thermocouple. Alumina runners were provided inside of the reaction tube to enable the quenching of the slags without any damage to the reaction tube. The gas mixture was lead into the reaction zone by a narrow alumina tube of 5 mm i.d. The gas was delivered in the hot zone of the furnace just above the samples in order to minimize the errors due to thermal segregation of the components in the case of the gas mixtures with components with varying densities. The temperature of the furnace was controlled by a programmable EUROTHERM 2408 regulator with a Pt-30 pct Rh/Pt-6 pct Rh thermocouple as the sensor with an accuracy of ± 3 K. The samples were heated in argon atmosphere at a heating rate of 3°C/min up to their liquids temperatures (which were previously determined by separate DTA studies). The argon gas was passed through a gas cleaning system in order to minimize the impurities. Some samples, cooled directly after melting in Ar atmosphere did not show any mass increase indicating that the oxygen levels in argon were quite low and no oxidation occurred during this period.

In the case of oxidation experiments, after the molten slag samples attained thermal equilibrium, the argon gas was replaced by the oxidant gas the flow rate of which kept at 200 ml/min. Some samples were quenched by pulling them to the cold end of the furnace with the gas flowing. Others were cooled in the furnace, at a cooling rate of 3°C/min. The samples were weighed before and after the experiments and the mass gains were registered corresponding to the experimental conditions.

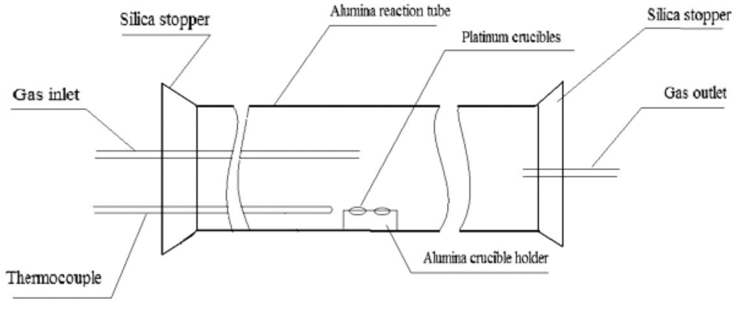


Figure 2: Illustration of the horizontal furnace

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were carried out in order to investigate kinetics of slag-gas reactions. The experimental assembly consists of an electronic microbalance with an accuracy of 3 μg mounted on a vertical furnace as shown in Figure 3.

An alumina reaction tube, (60 mm o.d. and 50 mm i.d.) was positioned in a vertical resistance furnace equipped with KANTHAL SUPER 1800 heating elements with a maximum working temperature of 1973 K. Platinum crucibles with 12 mm inside diameter and a height of 10 mm were used as the containers for the slag samples. The platinum crucible was filled in with the slag so that the slag level was close to the crucible top. The crucible was filled in with slag to the same level in all the experiments so that the results are comparable. The platinum crucible was suspended from the balance with a Pt-suspension wire which was taken out through a silicon stopper. The top end of the reaction tube was water-cooled. Radiation shields were used inside of the furnace in order to enhance the even temperature zone of the furnace as well as to prevent heat radiation to the furnace top. The length of the Pt wire was adjusted so that the sample was positioned in the even-temperature zone of the furnace. The sample was carefully centered in the alumina tube to ensure that neither the sample nor the suspension wire came into contact with the walls of the reaction tube. The sample temperature in the furnace was monitored by a calibrated Pt-30 pct Rh/Pt-6 pct Rh thermocouple positioned close to the bottom of the crucible. The oxidant gas was led into the reaction zone by a narrow alumina tube of 5 mm i.d. from the top of the furnace, minimizing the thermal segregation in the case of a gas mixture. The temperature in the furnace was controlled by a programmable regulator with a Pt-30 pct Rh/Pt-6 pct Rh thermocouple as the sensor to an accuracy of ± 3 K. The furnace was heated to the required temperature under constant argon flow. When the experimental temperature was reached, the platinum crucible with the synthetic slag was introduced into the even temperature zone of the furnace. The oxidant gas was then introduced in to the system at flow rate equal 400 ml/min. The reaction was allowed to proceed for about an hour during which the mass change and the temperature of the sample were registered every 2 min. When the mass of the sample became constant, the sample was quenched by lifting the sample up to the cold part of the furnace.

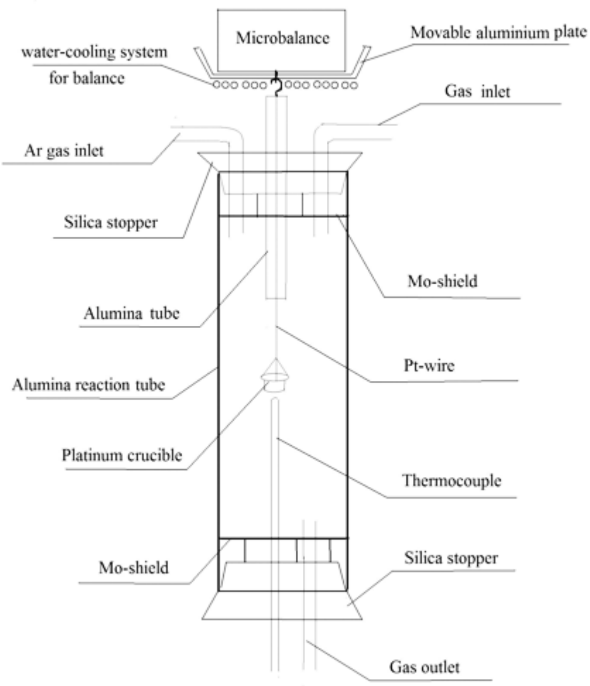


Figure 3: A schematic diagram of the TGA unit

X-Ray Diffraction

For the X-Ray Diffraction (XRD), a Siemens D5000 X-ray Irradiation Apparatus, with a copper Kα X-ray source was used. Parameters for the measurements were: scanning speed - 0,5°/min; scanning step- 0,02°; scanning angle 20° - 80°. Current and the voltage were set to 40 mA and 40 kV respectively. Peak analysis was carried out with the EVA software for Windows 95.

RESULTS AND DISCUSSION

Thermodynamic Analysis

The results of thermodynamics calculations are presented in Figure 4. It is to be noted that the calculations were carried out for oxides or fayalite and have not been extended to complex silicate solutions where the activity of the iron oxide had to be considered. This was in view of the preliminary nature of the calculations. The chemical reactions for which the Gibbs energy changes were computed based on literature data [7] were the following.

$$6FeO+O_2=2Fe_3O_4 \quad (2)$$
$$4Fe_3O_4+O_2=6Fe_2O_3 \quad (3)$$
$$6FeO(SiO_2)_3+O_2=2Fe_3O_4+3SiO_2 \quad (4)$$
$$3FeO+CO_2=Fe_3O_4+CO \quad (5)$$
$$2Fe_3O_4+CO_2=3Fe_2O_3+CO \quad (6)$$
$$3FeO(SiO_2)_3+CO_2=2Fe_3O_4+3/2SiO_2+CO \quad (7)$$

Calculations show that reactions 5-7 in the direction as written are hardly possible in a closed system, while reactions 2-4 are thermodynamically favoured.

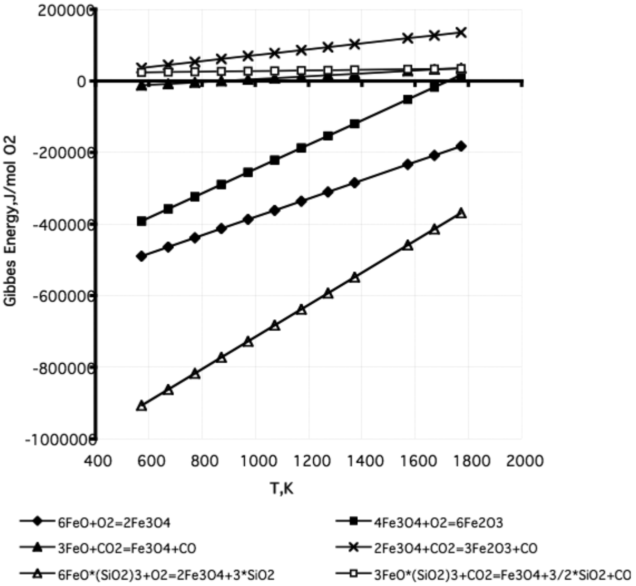


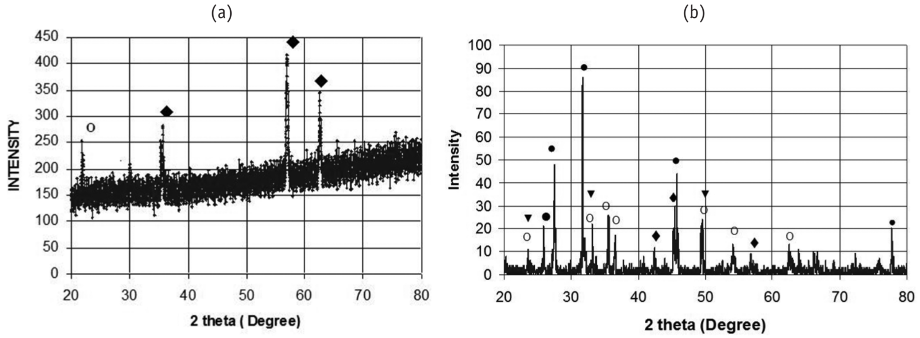
Figure 4: Relation between Gibbs Energy (J/mol O_2) and temperature (K)

XRD Analyses of the Samples from Horizontal Furnace Experiments

First experiment was done with binary system ($2FeOSiO_2$) at temperature 1823 K in air. The result shows very clearly that most of iron has been oxidized to magnetite (Figure 5, a).

Next series of experiments was carried out with ternary system CaO-FeO-SiO_2 in the range 1623-1723 K in air as well as a mixture of air and CO_2 gas. Figure 5, b presents the XRD analysis of the sample oxidized at 1623 K in air atmosphere. Oxidation products consist of magnetite, hematite, calcium silicate and even calcium ferrite.

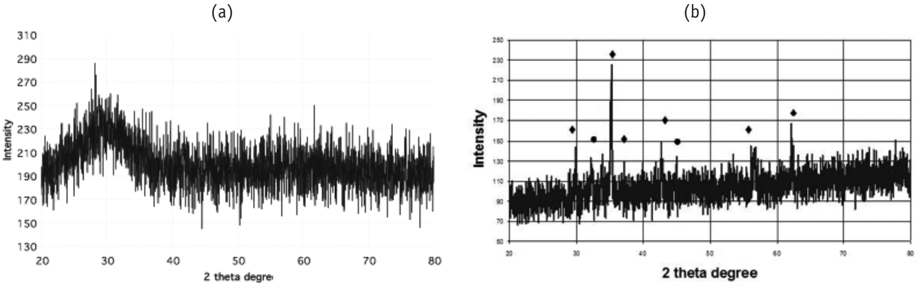
XRD analysis results showed, in general, that all the iron in nonmagnetic form was oxidized to magnetite. Peaks on the XRD pattern showed different phases - magnetic and non-magnetic, which can be separated. The fast quenched samples showed the presence of an amorphous phase (Figure 6a).



o - Fe_2O_3 (rhombohedra); □-Fe_3O_4 (FCC); • -$CaSiO_3$; ▼- $Ca_2Fe_2O_5$

Figure 5: XRD analysis: a) sample 1, table 1; b) sample 2, table 1

With increasing basicity, more magnetite was obtained which could be confirmed in TGA experiments. Very slight difference was observed between samples which were fast cooled after 1 and 3 hours indicating thereby that the oxidation process came to completion already after the first hour. Addition of CO_2 to the oxidant gas was found to arrest the oxidation reaction between magnetite and hematite as observed by the final mass increase. For industrial slags, XRD analyses showed that FeO is totally oxidized to magnetite (Figure 6b).



□-Fe304 (FCC); •-CaSi03

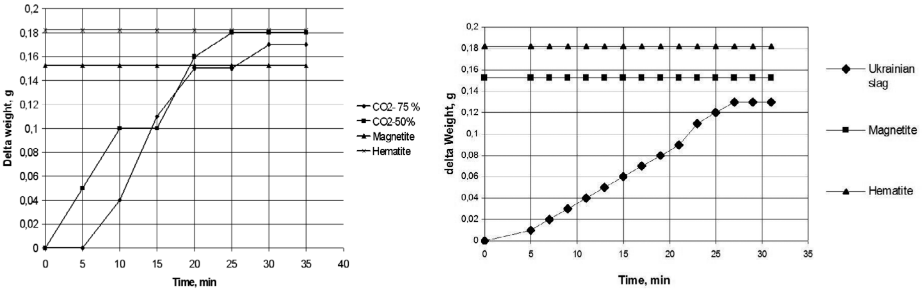
Figure 6: XRD analysis : a) sample 3, table 1, fast cooling; b) industrial slag, sample 7, table 1

Thermogravimetric Analysis

The oxidation process takes 20-25 min approximately. The oxidation reaction is faster and approaches complete oxidation with increasing temperature.

From the data represented at Figure 7a it is possible to see that with application of CO_2 /air mixtures below 1623 K temperature, steps of oxidation process could be controlled. With increasing CO_2 content in the oxidation atmosphere, the partial pressure of oxygen would decrease and oxidation process would consequently become slower and would lead to lower degree of oxidation so that the final produce was a mixture of magnetite and hematite. In the Figures 7-8, the magnetite and hematite lines shown represent the mass change if all FeO in the slag would be oxidized to magnetite and hematite respectively.

FeO in the industrial slag was found to be oxidized to a level close to magnetite (Figure 7b).



(a) (b)

Figure 7: TGA curves for oxidizing of: a) synthetic slag of different gas mixtures; b) industrial slag in air

With increasing basicity of the sample, the magnetite content after oxidation was found increasing (Figure 8), which can be explained by interaction of CaO and SiO_2 of iron silicates.

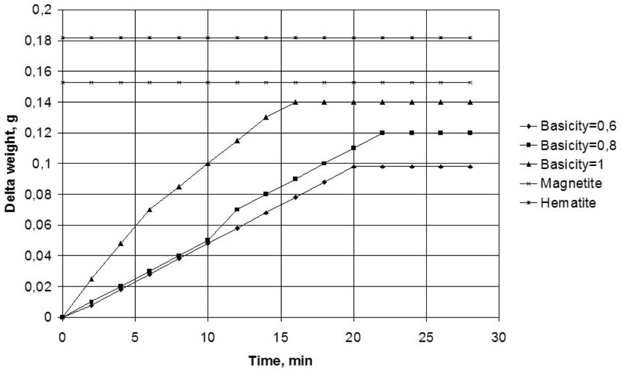


Figure 8: TGA results for synthetic slag

The activity of FeO generally increases with basicity facilitating the oxidation of FeO. The results of the XRD analysis showed peaks of calcium silicate along with peaks of magnetite.

The efficiency of the oxidation process for the industrial slags and synthetic slags was calculated by follow Equation:

$$k = [m_r / m_o] \times 100 \; ; \qquad (8)$$

The efficiency of the oxidation process was correlated with activity of FeO (Figure 9). Activity of FeO was estimated with application of *ThermoSlag software version 1.5 Copyright 2001 by KTH and USTB*. The standard state for FeO was chosen as liquid at the experimental temperature. The efficiency of the process was plotted as a function of the activity of FeO in Figure 9. The equation corresponding to this line in Figure 11 can be represented as:

$$k = 58.436\, a_{FeO} + 37.155, \; R^2 = 0.9752 \qquad (9)$$

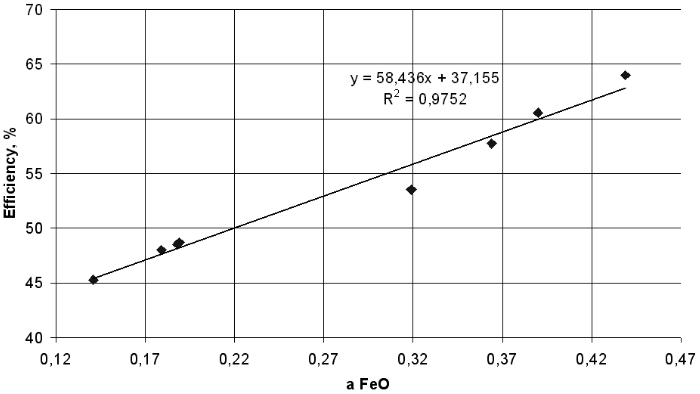


Figure 9: Relationship between the activity of FeO in the slag and efficiency of the process (%)

By using the Equation (9), it is possible to predict the activity of FeO in unknown metallurgical slag, if efficiency of the process could be measured. Conversely, if the activity of FeO in the slag system is known,- the efficiency of the process can be predicted by using the above Equation.

CONCLUSIONS

In the current work, the efficiency of slag utilizing by selective recovery of value added components by oxidation of its non magnetic iron compounds to magnetite has been investigated. Thermodynamic calculations demonstrate the feasibility of the oxidation route. Oxidation experiments were carried out in the case of synthetic (binary and ternary slag system) as well as industrial steelmaking slags containing iron bearing compounds. The XRD - evaluation showed clear peaks of magnetite for all the samples. The results for ternary system also indicate that, under specific experimental conditions, hematite and other compounds could be obtained.

The TGA investigations shows very clearly a strong effect of temperature and chemical potential on the oxidation process. With increasing temperature, hematite formation can be possible in ternary system. It is shown that the magnetite formation can be controlled by adjusting the partial pressure of oxygen. It was also shown that, with increasing basicity and % FeO in the system, the oxidation process was more effective towards magnetite formation. A linear correlation was found between thermodynamic activity of FeO and the oxidation efficiency

NOMENCLATURE

k = The efficiency of the oxidation process, %.

m_o = Rated mass changes, occurred when all the iron in the slag is oxidized to the magnetite, g.

m_r = Real weight gain, g.

ACKNOWLEDGEMENT

Partial financial support to this work from Swedish Foundation for Strategic Environmental Research, MISTRA through Swedish Steel Producers Association, Jernkontoret, is gratefully acknowledged.

REFERENCES

Pioro, L. S. & Pioro, I. L. (2004). *Reprocessing of Metallurgical Slag into Materials for the Building Industry*. Waste Management (24), pp. 371–379. [1]

Syshenko, A. V. & Ganoshenko, V. I. (2002). *Regeneratsiya Droblenogo Shlaka V Kislorodno-Konverternom Prostesse*. Metallurgicheskaya i gornorudfnaya promyshlennost (7), pp. 114-116. [2]

Alanyali, H., Col, M., Yilmaz, M. & Karagoz, S. (2006). *Application of Magnetic Separation to Steelmaking Slags for Reclamation*. Waste Management (26), pp. 1133–1139. [3]

Mikhail, S. A. & Turcotte, A. M. (1995). *Thermal Behaviour of Basic Oxygen Furnace Waste Slag*. Thermochimica Acta (263), pp. 87-94. [4]

Del Fabbro, M., Stefanutti, M. & Ceschia, C. (2001). *Nuovi prodotti dalla lavorazione delle scorie di forno ad areo elettrico: Caratteristiche fisico-chimiche e possibili impieghi in campo geotecnico-stradate*. Quarry and Construction settembere, pp. 81-91. [5]

Podorska, D. & Wypartowicz, J. (2008). *Thermodynamic Analysis of Elementary Processes in Molten Oxide Slag Reduction*. Archives of metallurgy and materials, vol. 53, pp. 595-600. [6]

Kazachkov, E. A. (1988). *Raschety po teorii metallurgicheskih protsessov*. M.: Metallurgiya, p. 288. [7]