Recovery of iron and manganese values from metallurgical slags by the oxidation route

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Doctoral Thesis

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ABSTRACT

In the modern practice, a sustainable development strategy in a domain of waste utilization is shifting its focus from a general completeness of recycling to a more specific attention to efficiently utilize elements in the wastes. This is well-illustrated by the steelmaking slag industries. The major waste product from the steelmaking practice is slag and its main constituents are: CaO, SiO$_2$, Al$_2$O$_3$, MnO, FeO and so on. The main field of application for the steelmaking slags is civil engineering, especially for road and waterway construction. However, a significant amount of the slag remains in the dumps, damaging the environment as well as requiring a land for secure storage. Efficient recycling of these materials is of increasing interest worldwide as a result of increasing sustainability in processes with respect to increasing raw material costs and waste reduction.

In order to find a practical solution, joint efforts are currently made at the Royal Institute of Technology, Sweden and National Metallurgical Academy of Ukraine. The concept is based on transformation of non-magnetic wüstite (FeO) to magnetic magnetite (Fe$_3$O$_4$) using an oxidizing atmosphere was proposed.

In order to verify the feasibility of the proposed way of slag utilization, experiments on the ternary CaO-FeO-SiO$_2$ and quaternary CaO-FeO-SiO$_2$-MnO slags systems, accompanied by thermodynamic and kinetic modelling, were performed. The crystal precipitation during synthetic slag oxidation was observed by Confocal Scanning Laser Microscopy (CSLM). Precipitated phases were found to be magnetite and manganese ferrite in the spinel form.

Obtained magnetite and manganese ferrite can be separated from the slag by magnetic separation.

The formation of nanosize manganese ferrite from the CaO-FeO-SiO$_2$-MnO slag system during oxidation was investigated. Experiments were conducted in a horizontal resistance furnace in an oxidizing atmosphere (air). The final product was analysed by X-ray diffraction (XRD). The particles size of the manganese ferrite was estimated by the Scherrer formula and was found to be of the order of 23-25 nm. In order to get an understanding of the magnetic properties of the manganese ferrite recovered from slag treatment, it was necessary to synthesize a reference compound from pure precursors. The MnFe$_2$O$_4$ nanopowder was synthesized by the oxalate route. The size effects on the magnetic properties of manganese ferrite particles were investigated.
The potential way of the magnetite particles separation from liquid slags was investigated by cold model studies. The experimental technique of mobilising non-conducting, nonmagnetic particles in conducting liquid in crossed electric and magnetic fields was investigated in order to find the way of the particle separation from the liquid steelmaking slags. The effects of the current density, magnetic field, size and shape of the particle on the particle velocity under action of the electromagnetic buoyancy force (EBF) in the electrolyte were analyzed.

**Key-words:** oxidation, metallurgical slag, recycling, FeO, iron recovery, manganese recovery, manganese ferrite, nano-ferrites, oxidation process, TTT, crystallization, kinetics studies, thermodynamic studies, modelling, cold-model studies, electromagnetic buoyancy force (EBF).
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Anna Semykina, Volodymyr Shatokha, Masanori Iwase, Seshadri Seetharaman

Supplement 2: “Confocal Scanning Laser Microscopy studies of crystal growth during oxidation of a liquid FeO-CaO-SiO₂ slag”

Anna Semykina, Jinichiro Nakano, Seetharaman Sridhar, Volodymyr Shatokha and Seshadri Seetharaman

Supplement 3: “The kinetics of oxidation of liquid FeO-MnO-CaO-SiO₂ slags in air”

Anna Semykina

Supplement 4: “Confocal Microscopic Studies on Evolution of Crystals during oxidation of the FeO-CaO-SiO₂-MnO Slags”

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Supplement 5: “Investigation of the potential way of the magnetite particles separation from liquid EAF slags”


Supplement 6: “Recovery of manganese ferrite in nanoform from the metallurgical slags”

Anna Semykina, Seshadri Seetharaman

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Anna Semykina, Lyubov Belova, Seshadri Seetharaman
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Related to this thesis publications:


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Supplement 1: Literature survey, calculations, experimental work, analysis and evaluation of experimental results, and major part of the writing.

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INTRODUCTION

During the production of iron and steel, large amounts of industrial wastes are generated as by-products. Efficient recycling of these materials is of increasing interest worldwide. The major solid waste product of the steelmaking industry is slag and its main constituents are: CaO, SiO$_2$, Al$_2$O$_3$, MgO, FeO, MnO and others. The main field of application for steelmaking slags is civil engineering, especially road and waterway construction [1]. However, significant amount of the slag (40 %) remain in the dumps, damaging the environment and requiring a land for storage [2, 3].

In Ukraine, under conditions when pig iron with relatively high Si content (0.9 % as average) is produced in blast furnaces, the slag yield in steelmaking reaches 100-110 kg/t [4]. For the existing steelmaking capacities, it equals to 3.9-4.1 million tons of slag per year. The slag contains 44-56 % of CaO and 15-33 % of FeO and is therefore very valuable material; for example, the yearly volume of the steelmaking slag contains up to 1 million ton of iron in the form of oxides (non-magnetic) 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 slag stored during the last century of industrial era in Ukraine, it is evident that development of the efficient solutions for steelmaking slag utilisation is extremely important.

Conventional approach envisages removal of only metallic iron from the slag by magnetic separation. The non-magnetic part of the slag is mainly utilised directly as the component for blast furnace burden, or as an additive to the sintering mixture. However, the slag contains also up to 12-17 % of SiO$_2$ which is unwanted compound for ironmaking yielding more slag and increasing coke consumption. Thus, conventional scheme does not solve the problem of efficient slag utilisation. It does not also match the principle of Sustainable Development Strategy and, in fact, even increases the volume of wastes produced in the neighbouring industries (iron- and coke-making).

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 constrained with the tendency to disintegration [5, 6]. Even though the methods to prevent disintegration are developed, the iron values remain in the slag in the form of unrecovered oxides.

A similar problem has been also considered in the Swedish steel industry. For example, the first slag in an Electric Arc Furnace (EAF) at Uddeholm Tooling AB in Hagfors,
Sweden, contains up to 30 wt% of wüstite. It is imperative that the iron value is recovered for recycling and the rest of the slag is used for civil engineering purposes. In order to find a practical solution, joint efforts are currently made at the Royal Institute of Technology, Sweden and National Metallurgical Academy of Ukraine.

1. RECOVERY OF METAL VALUES FROM METALLURGICAL SLAGS

1.1. Background

A sustainable approach to utilize steelmaking slag components based on transformation of non-magnetic iron monooxide to magnetite by oxidation has been proposed by the current author [7]. Air can be used to produce an oxidizing atmosphere. This allows selective recovery of iron-bearing and non-iron-bearing slag constituents for the specific purposes. From the technological point of view, pre-treated slag is processed using a magnetic method wherein iron oxides transformed to a magnetic form are separated for further utilization. The rest of the slag (non-magnetic) could be effectively used in production of cement binder or in other applications. Magnetic products may be utilized as a component for sintering mixture or for pelletizing iron ores.

Proposed concept for slag utilization can be used not only to recover iron compounds in the slag. It can be effectively applied to recover other metals such as manganese, vanadium, chromium and so on.

Some typical compositions for chromium, vanadium alloyed steel slags are:

for Ukraine steel industry: 25-29% SiO$_2$; 32-34% MgO; 20-22% Al$_2$O$_3$; 11-14% CaO; 2-3%Cr$_2$O$_3$; 0.5-1% FeO;
for Swedish steel industry: 28.0-41.4 %CaO; 4.8-4.98% MgO; 2.1-3.29% Al$_2$O$_3$; 9.5-10.44%SiO$_2$; 23-42.7%FeO; 4.98-5.1% MnO; 3.25-6.1% Cr$_2$O$_3$ and up to 5.0% V$_2$O$_5$.

The corresponding chemical reaction for oxidation can be written as:

\[ 2\text{FeO} + \text{MnO} + \frac{1}{2}\text{O}_2 \text{(air)} = \text{MnFe}_2\text{O}_4 \]  \hspace{1cm} (1)

\[ 2\text{FeO} + \text{V}_2\text{O}_5 + \frac{1}{2}\text{O}_2 \text{(air)} = 2\text{FeVO}_4 \]  \hspace{1cm} (2)

\[ \text{MO} + 2\text{CrO}_x + \left(\frac{(3-2x)}{2}\right)\text{O}_2 \text{(air)} = \text{MCr}_2\text{O}_4 \]  \hspace{1cm} (3)
The final products after oxidation are ferrites, which can be separated by magnetic separation methods for further utilization.

Preliminary experiments were carried out by the present author in order to examine the feasibility of the oxidation route towards the recovery of iron from liquid synthetic slags [8]. Synthetic (binary and ternary slag system) as well as industrial steelmaking slags were used in the experiments. Air and CO₂ gas were chosen as gas phase oxidants. The horizontal furnace and constructed thermogravimetric unit were adopted for the experiments. Analysis of the reaction products was carried out using X-ray diffraction method. The feasibility of a process for transforming the non-magnetic iron-bearing compounds to magnetite in the steelmaking slag by oxidation was demonstrated.

The present work investigates the mechanism of oxidation of FeO- and MnO-containing molten slags.

1.2. The oxidation concept
1.2.1. Thermodynamic basis

Prior to the design the experiments, thermodynamic calculations were carried out, with a view to estimate possibility of the oxidation route towards iron and manganese values recovery from liquid slags. During the oxidation of molten CaO-FeO-SiO₂ and CaO-FeO-SiO₂-MnO slags in an environment oxidizing enough to increase the valence of Fe, following reactions may take place:

\[ 3(\text{FeO})_{\text{slag}} + 1/2\text{O}_2 = (\text{Fe}_3\text{O}_4)_{\text{solid}} \]  
\[ 2(\text{FeO})_{\text{slag}} + 1/2\text{O}_2 = (\text{Fe}_2\text{O}_3)_{\text{solid}} \]  
\[ 2(\text{FeO})_{\text{slag}} + (\text{MnO})_{\text{slag}} + 1/2\text{O}_2 = (\text{MnFe}_2\text{O}_4)_{\text{solid}} \]

In the entire thesis, FeO is considered as stoichiometric. The nonstoichiometry of “FeₓO” decreases in silicate melts and Fe²⁺ gets stabilized. Thus, the assumption that all Fe is present as Fe²⁺ is reasonable. In order to find out what phases can be obtained in the current oxidation atmosphere, thermodynamic calculation was performed by using FactSage 6.1 ((Thermfact Ltd. (Montreal, Canada) and GTT Technologies (Aachen, Germany)). As an example Figure 1 and Figure 2 represent a phase diagram, temperature
vs. partial pressure of oxygen in the ternary system 35% CaO, 30% FeO, 35% SiO$_2$ and quaternary system 27.5% CaO, 30% FeO, 15% MnO, 27.5% SiO$_2$ respectively.

![Phase Diagram](image)

Figure 1. Temperature-partial pressure of oxygen phase diagram for ternary system. Line marked (A) corresponds to the partial pressure of oxygen in air. P(O$_2$) presented in Pa.

It is seen in Figure 1 that, at approximately 1600 K, the slag occurs as homogeneous liquid phase at the oxygen partial pressure equal to oxygen partial pressure in air. As the system is cooled to temperature below 1600 K calcium silicate can be obtained in the liquid slag. Hematite and calcium silicate can form in the liquid slag over a temperature range of 1530K -1560K.

From Figure 1, it can be also seen that over a range of $\log_{10}(P(O_2)) = -3.0$ through 2.0, FeO in the slag may be oxidized to magnetite ($< 1560$K). To produce magnetite, it is advantageous to use a lower partial pressure of oxygen rather than in air (e.g., CO$_2$ gas or CO$_2$/air mixture).
Figure 2 shows temperature vs. partial pressure of oxygen in the quaternary system. At the low partial pressure of oxygen \(\log_{10}(P(O_2))=-5\) and temperature range of 1430K-1607K, the slag is molten. With the introduction of the oxidant gas, \textit{viz.} air, \(Fe^{2+}\) in the slag changes its valence and, depending upon the temperature, different phases are precipitated. It is seen in the figure that, in air, in the temperature range of 1548K - 1607K, only spinel may be thermodynamically obtained from the liquid slag due to oxidation. The main constituents of spinel are manganese ferrite and magnetite. From this diagram, it easy to predict, that to obtain manganese ferrite or magnetite as a final product after slag oxidation in air, it is necessary to work in the temperature range 1548K - 1607K.

Before conducting experiments for all the experimental slag compositions, similar type of thermodynamic calculations was performed. On the basis of obtained data, the experimental conditions were chosen (temperature and partial pressure of oxygen).
1.2.2. Kinetic background. Mechanism of oxidation involved

During the thermogravimetric studies by the present author, the isothermal mass change curves showed differences in slopes at different stages of oxidation indicating a change in mechanism as the reaction progressed [9]. Oxidation may take place by steps, starting first with an incubation period (corresponding to the initial oxygen dissolution in the slag), then, the chemical reaction rate-controlling step (corresponding to a linear part of the slope), and finally, diffusion of iron/manganese/oxygen rate-controlling step (corresponding to the parabolic part of the slope). The three steps of the oxidation reaction would correspond broadly to the three slope changes in a typical thermogram as presented in Figure 3.

![Figure 3. Illustration of the three plausible steps in the oxidation mechanism marked on a typical thermogram.](image)

The region where the transition from chemical control to diffusion control is marked in the figure as “mixed control”.

A. Initial oxygen dissolution as rate-controlling step

With the onset of the oxidation process, the oxygen molecules impinge on the slag surface leading to the oxidation of FeO in the slag. Reaction (4-6) would be occurring at the gas/slag interface.

As the oxidant gas is let in, the thermograms show an incubation period, which is likely to correspond to the initial dissolution of oxygen in the slag.

In the present work, an attempt was made to describe this incubation period by an Avrami-type of equation [10].
This equation can be rearranged to linear form by expressing in logarithmic terms:

\[ \ln(\ln \frac{1}{1-X}) = \ln K_N + n \ln t \]  

where \( X \) is the reacted fraction, \( K_N \) is a constant (can be determined graphically), \( t \) is the time, s.

### B. Chemical reaction rate-controlling step

At the initial stage, the effect of the product layer formed is less significant and chemical reaction would be the rate-controlling step. The main equation corresponding to the chemical reaction control step can be expressed as:

\[
\frac{\Delta m}{A} = \Omega \exp\left(\frac{-\Delta E_a}{RT}\right)t
\]

where \( \Omega \) is a pre-exponential term; \( \Delta E_a \) - Arrhenius activation energy, \( t \) is time in s.

By plotting the term on the left-hand side of equation (9), viz. \( (\Delta m/A) \) at different temperatures as a function of time, the coefficient \( \eta \) (which is defined as \( \eta = \Omega \exp\left(\frac{-\Delta E_a}{RT}\right) \)) can be estimated from the slope. From the Arrhenius plot, where \( \ln \eta \) is function of \( 1/T \), the activation energy for the chemical reaction rate-controlling step could be evaluated.

### C. Diffusion as rate-controlling step

An analytical description of diffusion as the rate-controlling step is based on the concept that during the oxidation of liquid slag in air a porous solid product layer will be formed. The formation of such a product layer was confirmed during experiments in the case of the quaternary MnO-CaO-SiO₂-FeO system. The size of the pore was estimated to be varying from 1.0 µm to 5 µm [11].

The oxidation reaction would result in a build-up of the product magnetite/hematite/manganese ferrite layer. The product layer covers the surface of the slag so that the oxidation process at later stages is likely to be controlled by diffusion of oxygen through the product layer. A schematic illustration of the oxidation phenomenon is presented in Figure 4. It is seen that a layer of the product is formed on top of the molten slag. As diffusion progresses, the oxygen potential at the top and the bottom of
this product layer would be different, the former closer to the oxygen potential of the
gas phase, depicted in the figure as $C_{O^{'}}$ and the latter to that of the equilibrium oxygen
potential prevailing between the slag and the product layer, $C_{O^{'}}$ in the figure.

![Figure 4. A schematic illustration of the oxidation phenomenon.](image)

The possible transfer steps that may occur during this stage of the oxidation process are:

1. Gas phase transfer of reaction species to the slag-gas interface
2. Transfer of reacting species through the product layer to the reaction front

The rate of oxidation may be controlled by one or a combination of these steps. The gas
phase diffusion may not have an impact on the reaction rate as the oxidation is carried
out with the flow of the oxidant above the starvation rate for the reaction. Thus step 1
above may be ruled out.

Considering step 2, increased growth of the layer by oxidation requires diffusion of
$Fe^{x^+}/Mn^{y^+}$ ions and/or $O^2-$ ions. These two diffusion processes can be described as
follows:

1. $Fe^{x^+}/Mn^{y^+}$ ions can diffuse from the liquid slag/product interface to the outer
   surface where they will react with the oxygen in the atmosphere to create more
   $Fe_3O_4/Fe_2O_3/MnFe_2O_4$. This would be accompanied by the transfer of electrons or
   “counter-current” diffusion of $O^2-$ maintaining charge neutrality.
2. Alternatively, $O_2$ molecules (through pores) or $O^2-$ ions can diffuse from the
   surface to the manganese ferrite/liquid slag interface where they will react with the
   $Fe^{x^+}/Mn^{y^+}$ to form more magnetite/hematite/manganese ferrite.

It was experimentally shown by the present author [11] that the oxide product layer had
pores.
As mentioned earlier, the diameter of the pores obtained from the SEM micrographs was about 2-5 \(10^6\) m. The mean free path of the oxygen molecule could be estimated by equation (10) as 1.6 \(10^{11}\) m.

\[ l = \frac{kT}{\sqrt{2P \pi d^2}} \tag{10} \]

where \(l\) is the mean free path of the oxygen molecule; \(k\) is a Boltzmann constant, J/K; \(T\) is a temperature, K; \(P\) is a pressure, Pa; \(d\) is a diameter of the oxygen molecule.

Thus, the pores would be wide enough to promote molecular diffusion of oxygen from the gas phase to the slag/product interface and thus, the contribution of Knudsen diffusion may be considered less significant.

With the progress of the oxidation reaction, the thickness of the layer would increase and steady state conditions would prevail.

Following mathematical expressions of the diffusion of oxygen through the product layer are described for the case of quaternary system oxidation by the reaction (6).

According to the Fick’s diffusion law, the diffusion rate of oxygen in the iron oxide layer can be expressed as:

\[ J = -D_o \left( \frac{dC}{dx} \right) \tag{11} \]

where \(J\), \(D_o\), \(C\) represent the flux, diffusion coefficient and concentration of oxygen in product layer, respectively, \(x\) is the distance along the direction of oxygen flux.

Rearranging this for the present case:

\[ \frac{dm_o}{dt} = AD_o \frac{C_o^i - C_o^f}{x} M_o \tag{12} \]

where \(A\) is the surface area, \(m_o\) and \(M_o\) are the mass and molar mass of oxygen, and \(t\) is the time.

Assuming that 1 mole of atomic oxygen produces 1 mole of manganese ferrite \(n_o = n_{MnFe_2O_4}\), then:

\[ m_o = \frac{m_{MnFe_2O_4}}{M_{MnFe_2O_4}} M_o \tag{13} \]

where \(m_o\) and \(m_{MnFe_2O_4}\), \(M_o\) and \(M_{MnFe_2O_4}\) are the mass and molar mass of oxygen and manganese ferrite respectively.
On the other hand:

\[ m_{\text{MnFe}_2O_4} = A \rho_{\text{MnFe}_2O_4} x \varepsilon \]

where \( \rho_{\text{MnFe}_2O_4} \) is the manganese ferrite density, \( \varepsilon \) is the manganese ferrite fraction in the product layer.

\[ m_o = \frac{A \rho_{\text{MnFe}_2O_4} x \varepsilon M_o}{M_{\text{MnFe}_2O_4}} \]

Differentiating the above equation with respect to time \( t \), one obtains:

\[ \frac{dm_o}{dt} = \frac{A \rho_{\text{MnFe}_2O_4} \varepsilon M_o}{M_{\text{MnFe}_2O_4}} \frac{dx}{dt} \]

Combining equation (12) and equation (16), we can write the following equation:

\[ x \frac{dx}{dt} = \frac{D_o (C_o' - C_o')M_{\text{MnFe}_2O_4}}{\varepsilon \rho_{\text{MnFe}_2O_4}} dt \]

Integrating the above equation with initial boundary conditions of \( x=0 \) when \( t=0 \), and rearranging the terms:

\[ x^2 = \frac{2D_o (C_o' - C_o')M_{\text{MnFe}_2O_4}}{\varepsilon \rho_{\text{MnFe}_2O_4}} t \]

Combining equations (15) and (18),

\[ \left( \frac{m_o}{A} \right)^2 = \frac{2 \rho_{\text{MnFe}_2O_4} \varepsilon M_o^2 D_o (C_o' - C_o')}{M_{\text{MnFe}_2O_4}} t \]

By applying ideal gas law, \( C_o' \) and \( C_o \) can be expressed as:

\[ C_o' = \frac{n}{V} = \frac{P_{O_2}}{RT} \]

\[ C_o = \frac{n}{V} = \frac{P_{O_2}}{RT} \]

where \( P_{O_2} \) is a partial pressure of oxygen in equilibrium with slag/MnFe_2O_4 phase boundary.

The mixed control step corresponds to a transition between the region where the chemical reaction is solely rate-controlling and the region where diffusion of oxygen ions through the product layer determines the reaction rate:

\[ J = l \cdot \left[ -D_o \left( \frac{dC}{dx} \right) \right] + q \Omega \exp \left( \frac{-\Delta E_a}{RT} \right) t \]

Where \( J \) is flux; \( l \) and \( q \) represent the contributions of the diffusion and chemical reaction, respectively, in the oxidation process.
Combining all the steps involved a complete mathematical description of the oxidation process can be given.

2. EXPERIMENTAL

2.1. Materials and Sample preparation

To produce wüstite (FeO), appropriate amounts of iron (< 10 µm, purity of 99.9+%), and Fe₂O₃ (< 5 µm, purity of 99+%) powders supplied by Sigma Aldrich Chemie, Germany were carefully mixed so that the final composition would correspond to that of (FeO) in equilibrium with iron at 1273 K. The mixture was compacted and placed in an iron crucible (purity of 99.9%), which was then maintained in an argon atmosphere at 1273 K in a vertical resistance furnace. The crucible was quenched after 24 hours. Produced (FeO) was examined by X-ray diffraction method (XRD) and the absence of both metallic iron and solid magnetite was confirmed. From the diffraction pattern, the lattice parameter of the (FeO) produced was computed to be 4.30 Å, which is in agreement with the literature value of 4.3088 Å [12]. Other materials used in the slag preparation, CaO powder with a purity of 99.9% and SiO₂ powder with a purity of 99.5%, MnO powder with a purity of 99.5% were also supplied by Sigma Aldrich Chemie (Germany). SiO₂ powder was dried for 24 hours at 1073 K and CaO powder at 1273 K for 2 hours in an Ar atmosphere prior to mixing.

2.2. EXPERIMENTAL TECHNIQUES ADOPTED

2.2.1. Confocal Scanning Laser Microscope (CSLM)

A hot-stage equipped Confocal Scanning Laser Microscope (CSLM) was used to investigate the dynamic phenomena at the micro-structural level during iron- and manganese-recovery from the liquid FeO-CaO-SiO₂ and FeO-CaO-SiO₂-MnO slags.

The experiments were performed with a confocal scanning laser microscope (Model 1LM21H, Lasertec). Details of the CSLM are available in the literature [13, 14]. A simplified schematic of the CSLM is shown in Figure 5, which indicates the experimental setup used for this study. A He-Ne laser with a wavelength of 632.8 nm was applied onto the sample surface where the focal point returned the brightest contrast and real-time high resolution images (up to 0.25 µm) can be obtained from the confocal optics. A sample is placed at one of the two focal points in the gold-coated elliptical furnace with a halogen lamp located at the other. In the experimental setup used, a cylindrical platinum crucible containing approximately 0.030 g of slag was placed on a high-density alumina
crucible. The whole sample was then set on a platinum sampler pan (10 mm diameter) as indicated in Figure 6.

Figure 5. Schematic description of CSLM with gold-coated heating chamber.

Figure 6. Platinum sample holder of the present setup.
Before the experiment, the chamber was evacuated for 10 min and was purged with argon gas for 20 min. Each slag sample in the Pt-crucible was then heated at the CSLM hot stage in an Ar atmosphere. In order to ensure to start from a completely molten slag, the sample was heated to 1773-1873 K until it completely melted, then slowly (5 K/min) cooled down to the aimed temperatures. Temperature of the samples was controlled by a computer-based program and continuously auto-adjusted to compensate exothermic and endothermic reactions. The oxygen partial pressure was changed to an oxidizing atmosphere when the atmosphere was switched from Ar to air at a flow rate of 200 ml/min. After 30 min of oxidizing, the sample was quenched to room temperature in an Ar atmosphere. The sample was then analyzed by electron scanning microscopy equipped with EDS.

Before experiments, the temperature calibration for the sample holder was carried out (see Figure 7). The second thermocouple was introduced close to the platinum crucible bottom. The reading from this thermocouple was assumed to be the actual temperature, while the built-in sample holder thermocouple was the set temperature. The sample (actual) temperature showed a negative deviation as compared to the holder temperature (set).

![Temperature Calibration Graph]

Figure 7. Temperature calibration for the Pt sample-holder.
2.2.2. Thermogravimetric Analysis (TGA)

The oxidation of FeO- and MnO-containing synthetic slags was investigated by thermogravimetric analysis (TGA) using SETARAM TAG 24 (France) and SETARAM TAG 92 (France) units.

A. SETARAM TAG 24 (France) unit

The experimental assembly consists of an electronic microbalance, a graphite furnace with two chambers (Figure 8) and a gas cleaning system (Figure 9). During the experiments, a platinum crucible containing pure, dehydrated alumina powder was hung from one of the balance arms while in the other, the slag sample having nearly the same mass was kept in a similar Pt crucible. The Al₂O₃ powder in the first chamber served as a reference sample for thermogravimetric analysis. The microbalance has a detection limit of 0.001 mg. The system is fully operated by a computer.

![Figure 8. Experimental setup for thermogravimetric analysis: 1-electronic microbalance; 2-carrier gas inlet; 3-gas controller; 4-thermocouple; 5-gas outlet; 6-Pt-basket for the Pt-crucible; 7-Pt-crucible; 8-vacuum pump; 9-graphite furnace.](image)

Platinum crucibles with 10.0 mm inner diameter and a height of 8.0 mm were used as the containers for the slag samples. In all the experiments, the same level of slag in the crucible was maintained so that the results are comparable. In order to ensure homogeneity, the slags were premelted.
The crucible was placed in a Pt basket suspended from the balance with a Pt wire and placed in the alumina reaction tube with 21 mm inner diameter kept inside a graphite furnace. The sample was positioned in the uniform temperature zone of the furnace and carefully centred to ensure that neither the sample crucible nor the suspension wire came into contact with the walls of the alumina tube. The furnace temperature was controlled by a programmable regulator EUROTHERM 2408 with a Pt-30 pct Rh/Pt-6 pct Rh thermocouple as the sensor providing a control accuracy of less than 1K. The thermocouples in the dual furnace system were positioned as closely as possible to the bottom of the crucibles. Before the experiments, the chambers with the sample and the reference were purged with purified argon for 24 hours. The furnace was then heated to the desired temperature at the rate of 20°/min, with Ar gas flowing at the rate of 0.15 l/min. The sample was kept at the target temperature for 3400 s in order to ensure the attainment of thermal equilibrium. No mass change was noticed during the heating or the soaking period ensuring thereby that the argon gas was neither oxidizing nor reducing to the slag sample. Ar was then replaced by the oxidant gas, air as the oxidation experiments were started.

B. SETARAM TAG 92 (France) unit

The experimental assembly with the gas cleaning system present on the Figure 10 and Figure 9. The system is fully operated by a computer.
The procedure of the experiment was similar to the earlier one. Before the experiments, the chamber with the sample was evacuated down to 10 Pa for 600 seconds and subsequently flushed with purified argon gas \((\lg(P_{O_2}) \approx -5)\). The furnace was then heated at 20 K/min to the desired temperature, with Ar gas flowing at a rate of 0.2 l/min. Ar was then replaced by the oxidant gas, air in the present experiments.

The starvation rate for the flow of the oxidant gas, \(\text{viz.}\) air was determined in the preliminary experiments. All the experiments were conducted in isothermal mode for duration of 1800 sec. The mass and the temperature of the sample were recorded every 1 sec. After the experiments, the samples were cooled in the furnace in an argon atmosphere at a maximum possible rate. Quenched samples were analysed by XRD and SEM-EDS.

2.2.3. Sample characterization: X-ray diffraction analysis (XRD), Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS)

For the XRD analysis, a Siemens D5000 X-ray unit, with a copper K\(\alpha\) X-ray source was used. SEM analysis was carried out in a JEOL SEM unit and SEM LEO 1530 unit with GEMINI column, Germany.
3. RESULTS AND DISCUSSIONS

3.1. Crystal growth studies by CSLM technique during oxidation of ternary FeO-CaO-SiO₂ and quaternary FeO-CaO-SiO₂-MnO slag systems

The present work investigates dynamic phenomena at the micro-structural level during iron- and manganese-recovery from the liquid FeO-CaO-SiO₂ and FeO-CaO-SiO₂-MnO slags using an oxidation method. A hot-stage equipped Confocal Scanning Laser Microscope (CSLM) was used to analyze the kinetic behaviour of crystallization in synthetic slags. Based on observed precipitations, a Time-Temperature-Transformation (TTT) diagram has been created. The crystallization studies were conducted in air.

The chemical compositions of the samples used in the experiments are presented in Table 1.

Table 1. Chemical compositions of synthetic slags obtained by chemical analysis.

<table>
<thead>
<tr>
<th>№</th>
<th>Composition, weight %</th>
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</tr>
<tr>
<td>5</td>
<td>35.0</td>
<td>30.0</td>
</tr>
</tbody>
</table>

* In the present work, basicity, B was defined as: $B = \frac{CaO}{SiO₂}$

Experimental assembly (CSLM unit) and procedure have been presented in the chapter “2. EXPERIMENTAL” of this thesis.

Successive CSLM images (top-down view) in Figure 11 show a typical crystal evolution at the gas/liquid interface for ternary system, which was found to occur at a certain time after argon gas was switched over to air. The time delay before the air reached the sample after switching was estimated to be approximately 30-40 seconds for a flow rate of 0.2 l/min.

In the beginning of the experiment, the powder sample (see Figure 11, a) was heated until it became completely molten in the argon atmosphere.

After melting, the sample was slowly cooled to the aimed temperature and the argon gas was switched on to air, while the temperature was maintained constant (Figure 11, b).
The first crystals were observed after 240 sec of air introduction (see Figure 11, c). With time, the crystals grew (Figure 11, d) and agglomerated (Figures 11, e and 11, f) with their sizes reaching 40-50\(\mu\)m in some cases. The observed crystal size in the beginning was \(\leq 4\ \mu\)m. Crystals obtained at different temperatures during oxidation of ternary system are presented in Figure 12.

Even in the case of the quaternary system, the particles at the gas/liquid interface were found to grow and agglomerate with time (see Figure 13, c-e).
Figure 13. CSLM images of sample no 3, treated at 1333 K: a) original powder form; b) molten; c) first crystals observed; e) crystals grow; f) approaching equilibrium.

The growth eventually slowed down as the system was approaching equilibrium, Figure 13,f. Different types of crystals were observed in a size range of 1-50 µm. Below 1473 K, crystals had a shape as presented in Figure 13, whereas above 1473 K, observed crystals had complicated geometry (see Figure 14).

Figure 14. CSLM images of the samples treated at temperatures higher than 1473 K. a-b) sample no 1, 1523 K; c) sample no 2, 1523 K.

For all the samples at higher temperatures, observed crystals were bigger as compared to those corresponding to lower temperature, and had different shape.
A variation of time before the crystal precipitation took place was observed in situ using the CSLM and recorded for various temperatures and compositions. The corresponding TTT diagram was then constructed as shown in Figure 15-16. Figure 15 showed the TTT diagram corresponding to the ternary FeO-CaO-SiO$_2$ slag system. Two curves were identified. A node of the lower curve seems to be located slightly below 1530 K where the fastest kinetics was found, whereas that of the upper curve seems to be located around 1560 K. As temperature was raised, slopes of these curves rapidly decreased, indicating that the crystals required longer times to form.

Figure 15. TTT diagram for the ternary FeO-CaO-SiO$_2$ system.

Figure 16 represents TTT diagrams for quaternary FeO-CaO-SiO$_2$-MnO slag systems. Basicity seemed to have an influence on the crystal precipitation (Figure 16,a). In this figure, it is seen that kinetics is very slow for B=0.6 at 1473 K whereas it is very fast for B=1 at the same temperature. The effect of the MnO content in the slag samples with the similar basicity, was rather limited (Figure 16,b). With increasing basicity in the system, the crystal precipitation occurred faster. It is therefore likely that it was an increase in activity of FeO and MnO in the slag, which facilitated the precipitation of FeO- and MnO-based phases.
Figure 16. TTT diagram for the quaternary FeO-CaO-SiO$_2$-MnO system: a) basicity effect; b) MnO effect.

At the same time, an increase in basicity in the studied range may decrease viscosity of the molten slag, which would aid mass transport and thus precipitation kinetics. Some samples from CSLM chamber were quenched and analyzed by SEM equipped with EDS.

3.1.1. SEM-EDS results of the quenched samples

A. Ternary CaO-FeO-SiO$_2$ slag system

Quenched samples from the CSLM chamber were analyzed by SEM-EDS. SEM images of the quenched samples of ternary CaO-FeO-SiO$_2$ slag system are presented in Figure 17. The resultant EDS analyses were summarized in Table 2.

Figure 17. SEM images for the samples quenched from: a) 1580 K; b) 1560 K; c) 1533 K.
Table 2. EDS results of the quenched from the CSLM chamber, corresponding to Figure 17.

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<td>Si</td>
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<tr>
<td><strong>Figure 17, b (1)</strong></td>
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<td><strong>Figure 17, c (1)</strong></td>
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Table 3. EDS results of the quenched samples from the CSLM chamber, corresponding to Figure 18.

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<td><strong>Figure 18, b (1)</strong></td>
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<td>Fe</td>
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<td><strong>Figure 18, b (2)</strong></td>
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<td><strong>Figure 18, c (1)</strong></td>
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<tr>
<td>O</td>
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<td>Mn</td>
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<td>Fe</td>
<td>15.20</td>
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<td>Total</td>
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B. Quaternary FeO- CaO -SiO₂-MnO slag system

SEM images in Figure 18 for quaternary slag systems show the presence of magnetite/manganese ferrite in spinel and calcium silicate as determined by EDS. For sample no. 3, Table 1, treated at 1333 K, the SEM image shows the presence of a crystal phase (see Figure 18,a) represented by small crystals, which are similar in size and shape. For the samples treated at 1523 K, crystals of spinel as well as calcium silicates with various size and shape were observed (see Figure 18,b,c).

![Figure 18. SEM images of: a) sample no 3 treated at 1333 K; b)-c) sample no 2 treated at 1523 K.](image)

The EDS analyses on crystals are presented in Table 3. Crystals shown by arrows have similar chemical results. In Figure 18, c, the magnetite/manganese ferrite crystal (spinel) likely first formed, followed by calcium silicate around it.

3.1.2. XRD analysis

For the ternary system, the thermogravimetric investigations were performed. The furnace-cooled samples from the TGA experiments were analyzed by XRD. Resulting XRD patterns are presented in Figure 19.
As can be seen from Figure 19, as temperature increases, the intensity of the hematite peaks becomes weaker. At the same time, the intensity of the calcium silicates peaks becomes stronger.

### 3.1.3. Discussion

#### A. Oxidation of a liquid ternary FeO -CaO-SiO₂ slag system

FeO in molten slags, when exposed to an environment oxidizing enough to increase the oxidation degree of Fe can be oxidized to magnetite or hematite. The reactions (4) and (5) may take place.

The oxidation process can be controlled by the following steps:
1) Nucleation of magnetite/hematite during the initial oxidation reaction.
2) Chemical reaction.
3) Oxidation due to diffusion of oxygen/iron through the product layer.
In order to find out what phases can be obtained in the current oxidation atmosphere, thermodynamic calculation was performed by using FactSage 6.1. Figure 1 represents a phase diagram, temperature $\nu s.$ partial pressure of oxygen in the system. As the experiment was conducted, the initial atmosphere was argon and hence, all liquid was initially homogeneous. After switching to air, the FeO was oxidized and, depending upon the temperature, crystals precipitated. In air, over a temperature range of 1560K-1600 K, calcium silicate can be obtained in the liquid slag (see Figure 1), which may correspond to the large crystals with different morphology (see Figure 12,a and 17,a).

According to the phase diagram, hematite and calcium silicate can form in the liquid slag over a temperature range of 1530K -1560K. The CSLM investigation at 1560K shows regular morphology of the crystals (somewhat cubic shape (see Figure 12,b and 17,b). The XRD analyses of the sample oxidized at 1560K showed presence of calcium silicate. EDS analyses of the quenched sample also indicated the presence of calcium silicate and iron oxide. Iron oxide may have formed first and then calcium silicate precipitated around it. At a temperature of 1533K (which corresponds to the border between two regions: solid Ca$_3$Si$_2$O$_7$, hematite, CaSiO$_3$ and liquid slag containing hematite and calcium silicate), similar types of crystals were found by CSLM. The XRD investigations confirmed the presence of hematite as well as calcium silicate at this temperature.

The TTT diagram shows a discontinuity in the temperature range of 1560K -1570 K, which corresponds to another phase formation (Hematite). The EDS analysis of the sample quenched from 1560 K showed more significant presence of iron oxide in precipitated crystals while that from 1580K mainly indicated the presence of calcium silicates. The XRD analyses of the sample oxidized at 1580K in air also showed more calcium silicates with less hematite, compared to lower temperatures. This is in agreement with FactSage 6.1 calculations. Taking into account the XRD and EDS analyses, it can be also assumed that iron ions may be dissolved in the calcium silicate [(Fe, Ca)$_x$SiO$_y$].

From Figure 1, it can be also seen that over a range of $\log_{10}(P_{O2}) = -3.0$ through 2.0, FeO in the slag may be oxidized to magnetite ($< 1560K$). To produce magnetite, it is advantageous to use a lower partial pressure of oxygen rather than in air (e.g., CO$_2$ gas or CO/CO$_2$ mixture).

Data obtained in the present study and previous experience of the authors allows offering following strategies aimed at maximizing the yield of iron in the form of magnetite:
1) To perform oxidizing at lower temperatures with subsequent quenching in neutral atmosphere as soon as first precipitates appear. It is possible to assume that in a solid phase, transformation of Fe$_3$O$_4$ to Fe$_2$O$_3$ will be slow.

2) To control partial pressure of oxygen with e.g. additives of CO$_2$ in order to tailor precipitation within the area where Fe$_3$O$_4$ is present among the solid products. Previous studies by the present author [8] have demonstrated this possibility.

3) Simultaneous processing of steelmaking and e.g. ferromanganese slag. It was found by the present authors that with manganese oxide in the synthetic slag system, magnetite can be obtained as spinel as well as manganese ferrite [4]. Manganese in the slag stabilizes the magnetite and arrests further oxidation to hematite, as it was found for the ternary system.

B. Oxidation of liquid quaternary FeO-CaO-SiO$_2$-MnO slag systems

During the oxidation of molten FeO-CaO-SiO$_2$-MnO slags in an environment oxidizing enough to increase the valency of Fe reactions (4)-(6) may take place. In order to further investigate the effect of MnO, FactSage 6.1 calculations were carried out for constituents in the spinel phase. The number of moles of magnetite and manganese ferrite in the spinel was correlated to temperature. Figures 20-23 show that for samples 1-3, the maximum amounts of manganese ferrite and of magnetite can be found in the spinel phase around 1423-1523 K.

Figure 20. Number of moles of constituents in spinel vs. temperature for 31.0%CaO-29.5%SiO$_2$-27.9%FeO-11.5%MnO (sample no 1, Table 1).
Figure 21. Number of moles of constituents in spinel vs. temperature for 28.8%CaO-28.7%SiO$_2$-26.5%FeO-15.8%MnO (sample no 2, Table 1).

Figure 22. Number of moles of constituents in spinel vs. temperature for 27.4%CaO-34.0%SiO$_2$-27.3%FeO-11.1%MnO (sample no 3, Table 1).
Figure 23. Number of moles of constituents in spinel vs. temperature for 21.9%CaO-37.0%SiO$_2$-29.5%FeO-11.5%MnO (sample no 4, Table 1).

For sample no 4, two peaks were found (see Figure 23); one corresponding to 1373 K where the maximum amount of manganese ferrite can be obtained in the spinel phase, and the other to 1523 K where magnetite dominates in the spinel. For the sample with maximum MnO and basicity equal to 1, maximal yield of manganese ferrite was determined by FactSage calculations (see Figure 21).

C. **Kinetic analyses of the crystal growth during oxidation of liquid FeO-CaO-SiO$_2$ and FeO-CaO-SiO$_2$-MnO slag systems**

There are three possible ways for crystals to grow on the slag surface (see Figure 24). First, the gas/solid interface can grow into gas when metallic species travel through the crystal to the interface where they react with oxygen. Second, when oxygen anions move through the crystal to the liquid/solid interface, such an interface moves into slag by interacting with metallic species. In the third scenario, the triple point where gas, liquid and solid meet can laterally grow without solid state diffusion involved. The growth can occur when the sufficient amount of metallic species and oxygen anions interact at the interface.
Provided that dissociation rates are comparative in all the three cases, growth at the triple point may occur most easily because of: a) larger interfacial energy; and b) faster diffusion in the gas phase (gas-phase mass transport) and in the liquid phase (liquid-phase mass transport). There are three possible rate controlling steps for this growth:

1. Gas-phase mass transport control: if it is assumed that $\text{Fe}^{x+}/\text{Mn}^{y+}$ is always sufficiently available at the interface, diffusion of $\text{O}_2$ controls the reaction rate.
2. Liquid-phase mass transport control: if $\text{Fe}^{x+}/\text{Mn}^{y+}$ requires long range diffusion and its supply is slow, the gas flow rate and gas-phase mass transport rate have a negligible effect on growth of crystals compared to diffusivity of $\text{Fe}^{x+}/\text{Mn}^{y+}$.
3. Mixed control of 1 and 2.

If sufficient amounts of iron/manganese species are assumed to be at the slag-gas interface, the crystals formation would depend on a mass transfer in the gas phase. However, kinetics cannot be explained by the gas-phase mass transport alone. To form crystals, a supply of both oxygen anions and iron/manganese species must be sufficient. Then, the diffusion of iron/manganese species through the liquid slag to the surface is an important step as well. Therefore, the nucleation event must be influenced by a balance of the gas-phase mass transport and liquid state diffusion of the mobile species, which counteract with one another over the temperature. The TTT diagram has a C-shape and the basicity has an influence on it, supporting the mixed control of the crystal growth.

The measured growth rates of the crystals during oxidation of the liquid $\text{FeO-CaO-SiO}_2$ and $\text{FeO-CaO-SiO}_2-\text{MnO}$ slags are shown in Figure 25.
Figure 25. The measured growth rates of the crystals at different temperatures: a) ternary FeO-CaO-SiO$_2$ slag system; b) quaternary FeO-CaO-SiO$_2$-MnO slag system.

Faster growth of crystals is observed at higher temperatures of the experiment. This could be indicative of a faster rate of transport in the liquid phase as a result of a lower viscosity.

The present TTT diagram for the crystal formation at the gas/liquid slag interface (see Figure 16) showed that, with an increase in temperature, the start of the precipitation is delayed as well. This could be caused by lower degree of super saturation for crystal precipitation as the temperature is increased.

3.2. Thermogravimetric investigations

Kinetic of the oxidation of liquid FeO-CaO-SiO$_2$ and FeO-MnO-CaO-SiO$_2$ slags in air was studied. Experiments were carried out using a thermogravimetric technique in an oxidizing atmosphere (air). Reaction products after oxidation were analyzed by X-ray diffraction analysis, optical and by Scanning Electron Microscopy equipped with an Energy Dispersive Spectrometer.

Experimental setup and procedure are shown in chapter “2. EXPERIMENTAL” of this thesis.

3.2.1. Oxidation of FeO containing liquid slags

The experiments were conducted in the temperature range of 1623K - 1773K. The slag compositions studied are presented in Table 4.
Table 4. Chemical composition of the slags studied and the temperature range of the experiments

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<th>№</th>
<th>Slag composition, weight %</th>
<th>Liquidus temperature by Slag Atlas, K*</th>
<th>Temperature range used in the experiments, K</th>
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</tr>
<tr>
<td>5</td>
<td>37.5</td>
<td>25.0</td>
<td>37.5</td>
</tr>
</tbody>
</table>

*In the case of Slag Atlas[15], the values were read off from the CaO-FeO-SiO₂ ternary phase diagram which should correspond to low oxygen partial pressures.

Typical experimental curves for the isothermal mass gain during oxidation at different temperatures are presented in Figure 26. In this figure, the horizontal lines indicate the theoretical levels corresponding to complete oxidation of Fe²⁺ in the slag to Fe³⁺ (theoretically corresponding to hematite) and even partial oxidation corresponding to magnetite stage. The characteristics of the curves demonstrate that during 10-15 min of the experiment, the oxidation level of 70-90% of oxidation to hematite stage was reached.

![Figure 26](image)

**Figure 26.** The isothermal mass changes curves for the composition: 25% FeO; 37.5% CaO; 37.5% SiO₂ for different temperatures, K. Horizontal lines indicate oxidation levels corresponding theoretically to magnetite and hematite levels.
It can be seen in Figure 26 that an increase of temperature in the range 1623K -1723K is followed by the progressive mass gain caused by oxidation. The maximum oxidation level achieved also increases for all the slags studied with rise in temperature.

However, at 1773 K, the oxidation behavior is somewhat different; oxidation proceeds rapidly in the early stage but slows down at the later stage. The final mass gain (i.e. oxidation level achieved) is below the corresponding levels at 1673K and 1723K. This pattern is more distinctly observed in Figure 27 showing the first derivative of the mass gain with respect to time represented as:

$$\frac{d\Delta W}{dt} = \frac{d(W_f - W_i)}{\Delta t}$$

(23)

where \(W_i\) is mass recorded at time \(t\) and \(W_f\), initial mass of the slag in mg, and \(\Delta t\) is time interval in s.

Figure 27. Differential oxidation rate with respect to time as a function of reaction time for the sample: 25% FeO; 37.5% CaO; 37.5% SiO\(_2\), 1: 1673 K, 2: 1723 K, 3: 1773 K.

To explain the divergence of the oxidation behavior at 1773K from the lower temperature experiments, the samples, cooled at the maximum possible cooling rate in the thermoanalyser after TGA experiments, viz. 25 °/ min. were studied by optical microscopy and the SEM.
Optical images are presented in Figure 28 while the SEM image corresponding to 1773 K is shown in Figure 29.

![Figure 28](image1.png)  ![Figure 28](image2.png)

**Figure 28.** Images of the sample surface (25% FeO; 37.5% CaO; 37.5% SiO$_2$), observed by optical microscopy, for the temperatures: a) 1673K; b) 1773K. Magnification:x250.

![Figure 29](image3.png)

**Figure 29:** Image obtained by SEM (x6000) for the sample treated at 1773K.

Different phases (magnetite, hematite, calcium silicates even calcium ferrites) were observed in the samples which were oxidized below 1773K. Pores and even cracks were observed in the product layer. On the other hand, in the sample oxidized at 1773K, optical microscopy images show monolite structure without cracks. By the SEM analyses of this sample shown in Figure 29, it was found that the layer formed on the sample surface has nonporous dense crystalloid structure. Furthermore, the surface layer contained mostly magnetite (and some hematite), as seen from XRD patterns in Figure 30,a. On the other hand, XRD analysis of the sample, oxidized at 1673K show a multiphase structure in the surface layer (Figure 30,b). The phases present are in agreement with the FactSage 6.1 calculations.
Figure 30. XRD pattern of the top layer of the sample (25% FeO; 37.5% CaO; 37.5% SiO₂):
a) 1773 K; b) 1673 K; o - Fe₂O₃ (rhombohedra); ♦-Fe₃O₄ (FCC); ●-CaSiO₃; ▼-Ca₂Fe₂O₅.

With increasing basicity of the sample, the degree of oxidation was found to increase (see Figure 31). This is likely to be due to the increase in the thermodynamic activity of FeO with increasing basicity of the slag, facilitating the oxidation of FeO. Figure 32 shows the oxidation curves for different FeO contents in the slag.

Figure 31. The isothermal mass changes curves for the 1673 K for different basicity, (FeO)=30%.
Figure 32. The isothermal mass changes curves for the 1673 K, basicity =1.0 for different (FeO).

For a slag with unit basicity, the oxidation level at 1673 K was found to increase with the increase of the FeO content in the slag. While the oxidation rates and final oxidation degree were somewhat similar for slags containing 25 and 30 wt % FeO, the slag containing 20 wt % FeO showed a lower degree of oxidation, as the thermodynamic activity will be quite low. FactSage 6.1 calculations show that the activity of FeO in this slag is about 0.03 as compared to 0.06 as in the case of other slags around 1700 K.

A. Degree of oxidation

The degree of oxidation for the synthetic slags was calculated by the following equation:

$$\xi = \left[ \frac{m_r}{m_o} \right] \times 100 \quad (24)$$

where:

$\xi$ - The degree of oxidation, %;
$m_o$ - estimated mass changes, occurred when all the iron in the slag is oxidized to the hematite, mg;
$m_r$ - real mass gain, mg.
The degree of oxidation was correlated with activity of FeO (Figure 33).

Activity of FeO was estimated using the FactSage 6.1. The standard state for FeO was chosen as liquid at the experimental temperature. The degree of oxidation was found to be a linear function of the thermodynamic activity of FeO in the liquid slag (standard state: pure FeO liquid) in the entire experimental temperature range. The equation corresponding to the line in Figure 33 can be represented as:

\[ \xi = 1513.9 a(FeO) + 4.032; \quad R^2 = 0.8 \]  

(25)

Equation (25) enables an approximate estimation of the activity of FeO in the slag system studied. Alternately, it is possible, from a knowledge of the thermodynamic activity of FeO in the slag, the rate of oxidation of Fe\(^{2+}\) in the slag. This approach is being currently verified in the case of multicomponent slag systems containing FeO.

### 3.2.2. Oxidation of FeO-; MnO-containing liquid slags

Experiments were carried out using a TGA unit in the temperature range of 1500K - 1600K in air. The slag compositions are presented in Table 5.
Table 5. Chemical composition of the slags studied

<table>
<thead>
<tr>
<th>№</th>
<th>Composition, weight %</th>
<th>Basicity*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>SiO₂</td>
</tr>
<tr>
<td>1</td>
<td>21.0</td>
<td>34.0</td>
</tr>
<tr>
<td>2</td>
<td>27.5</td>
<td>27.5</td>
</tr>
<tr>
<td>3</td>
<td>33.0</td>
<td>22.0</td>
</tr>
</tbody>
</table>

* In the present work, basicity, B was defined as: $B = \frac{CaO}{SiO_2}$.

 Typical experimental curves for the isothermal mass gain during oxidation at different temperatures are presented in Figures 34. It can be seen that an increase in temperature in the range of 1500K - 1580K promoted a progressive mass gain. With increasing basicity of the sample, the mass change was found to decrease (see Figure 35).

Figure 34. The isothermal mass change curves for the slag composition: 30% FeO; 15% MnO; 21% CaO; 34% SiO₂ at different temperatures.
Figure 35. The isothermal mass change curves for the 1550 K for different basicities.

Samples from the TGA chamber were analyzed by SEM. SEM images of the furnace-cooled samples are presented in Figures 36-38. With increasing basicity, the surface morphology was found to be different. Sample 2 with basicity of 1.0, treated at 1600 K, had more rough surface compared to sample 3 with basicity of 1.5 treated at the same temperature (see Figures 36,a-36,b). Also, the top layer of the sample was found to be porous (see Figure 37,a). The cross section of the sample is presented in Figure 37,b.

Figure 36. The SEM images of the samples cooled in the TGA furnace: a) sample 2, Table 5, basicity equal to 1, T=1600 K; b) sample 3, Table 5, basicity equal to 1.5, T=1600 K.
Figure 37. The SEM images of the samples cooled in the TGA furnace: a) sample 3, Table 5, basicity equal to 1.5, T=1600 K; b) cross section, sample 3, Table 5, basicity equal to 1.5, T=1600 K.

From Figure 37, the size of the pore was estimated to be varying from 1.0 µm to 5 µm. The elemental profile of the cross section was determined by SEM-EDS and is presented in Figure 38.

Figure 38. The elemental profile of the cross section of sample 3. Top of the sample (slag/gas interface) is presented as “0” on the x-axis.
As can be seen in Figure 38, the manganese ferrite formation occurs on the top of the sample (at the slag/gas interface) where Fe and Mn are concentrated. As the slag depth increased, the atomic percents of Fe and Mn decreased while Si and Ca increase, indicating the presence of the silicate slag.

According to the phase diagram (Figure 2), spinel and calcium silicate can form in the liquid slag over a temperature range of 1533 K-1548 K. The isotherm of 1533 K is a border between two regions: \( Ca_3Si_2O_7 + \text{spinel} + CaSiO_3 \) and slag + spinel + \( CaSiO_3 \). XRD investigations confirmed the presence of both calcium silicate and spinel (manganese ferrite and magnetite) at this temperature.

The XRD analyses of the samples at 1580 K showed presence of calcium silicates as well as manganese ferrite and magnetite as spinel (see Figure 39 and Table 6). Calcium silicate possibly formed during cooling in the furnace.

![Figure 39. The XRD plot for sample number 1 (according to Table 5), B=0.6: a – manganese ferrite; b-calcium silicate \((CaSiO_3)\); c-\(Fe_3O_4\); d-calcium silicate \((Ca_3Si_2O_7)\).](image-url)
Table 6. Phases identified by XRD analysis of the samples after oxidation.

<table>
<thead>
<tr>
<th>Sample No. From Table 1</th>
<th>Identified Phases (in Order of Intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (30% FeO; 15% MnO; 21% CaO; 34% SiO₂)</td>
<td>MnFe₂O₄; Fe₃O₄; CaSiO₃; Ca₃Si₂O₇</td>
</tr>
<tr>
<td>2 (30% FeO; 15% MnO; 27.5% CaO; 27.5% SiO₂)</td>
<td>MnFe₂O₄; CaSiO₃; Fe₃O₄; Ca₃Si₂O₇</td>
</tr>
<tr>
<td>3 (30% FeO; 15% MnO; 33% CaO; 22% SiO₂)</td>
<td>MnFe₂O₄; CaSiO₃; Ca₃Si₂O₇; Fe₃O₄</td>
</tr>
</tbody>
</table>

As can be seen from Table 6, in the present experimental temperature range, manganese ferrite/magnetite and calcium silicate phases were identified as the oxidation products. For sample 2 and 3, Table 5, the manganese ferrite phase was dominating.

To investigate details in the spinel phase, FactSage 6.1 calculations were conducted to show potential constituents of spinel formed during the MnO-CaO-FeO-SiO₂ molten slag oxidation in air.

Figure 40. Mass in gram of constituents in spinel vs. temperature for: a) Table 5, sample 1, 21%CaO-34%SiO₂-30%FeO-15%MnO; b) Table 5, Sample 2, 27.5%CaO-27.5%SiO₂-30%FeO-15%MnO; c) Table 5, sample 3, 33%CaO-22%SiO₂-30%FeO-15%MnO.
The masses in gram of magnetite and manganese ferrite in spinel were correlated to the temperature. Figures 40 show that, for samples 1 and 2, higher amounts of manganese ferrite and of magnetite were found in the spinel phase around 1450 K through 1550 K. For sample number 3, higher amounts of spinel were obtained even at temperatures lower than 1450 K.

Basicity seemed to have an influence on the spinel formation. For the sample with basicity 0.6, the amounts of manganese ferrite and magnetite formed are comparable (see Figure 40,a). For samples with basicity 1 and 1.5, the amount of manganese ferrite is dominating in spinel (see Figure 40,b and Figure 40,c).

Further, according to thermodynamic calculations, with increasing basicity in the sample, total amount of the spinel increases. Thus, it is likely that there was an increase in activity of FeO and MnO in the slag, which facilitated the precipitation of the FeO\textsubscript{x} and MnO\textsubscript{x} based phases. Figure 41 describes the activity relationship with temperature.

![Activity relationship with temperature](image)

Figure 41. The relationship between activity with temperature calculated using FactSage 6.1.

As can be observed from Figure 41, in the experimental temperature range 1500K - 1600K, the activity of MnO is higher than of FeO or close to it. With increasing temperature, the activities of FeO and MnO increase, promoting the oxidation process and mass increase of the sample (see Figure 34).
Figure 35, showed that sample number 3 has less mass increase than sample 1 and 2, thus the amount of spinel formed was lower. This can be explained from the morphology of the slag, which will be changed with basicity of the sample. Changed morphology is likely with the change of the kinetics of spinel formation.

3.2.3. An analytical description of the oxidation mechanism

The thermograms for oxidation showed an initial incubation period corresponding to the oxygen dissolution in the slag followed by a chemical reaction-controlled stage. At later stages, the reaction rate was controlled by diffusion. The mechanism of the oxidation process was described in detail earlier in chapter “1.2.2. Kinetic background. Mechanism of oxidation involved”, where the corresponding mathematical expressions were derived.

As an example, the composition 30% FeO; 15% MnO; 27.5% CaO; 27.5% SiO\textsubscript{2} in a temperature range of 1500 K - 1600 K was considered. The simulations of three rate-controlling steps are compared with the experimental results in Figure 42. In the calculations, it was assumed that oxidation occurs by the reaction (3). Parameters Do and density were estimated from experimental results.

![Figure 42: The isothermal mass changes curves for the composition: 30% FeO; 15% MnO; 27.5% CaO; 27.5% SiO\textsubscript{2} for different temperatures, K : — calculated by the combined kinetic model; o experimental data.](image-url)
3.3. Possible applications to recover vanadium from metallurgical slags

Vanadium is analogous to chromium and its oxide ends up in the slag phase during high alloy steel production. The content of the vanadium in the SSAB (Sweden) LD-slag alone is about 4000 ton per year. In a view of economical and environmental impacts, the extraction of vanadium and retention of it to the metallurgical cycle is necessary. As mentioned earlier, recovery of valuable metals from slag phase by the oxidation route can be extended to other metals such as manganese, vanadium and chromium.

Chapter “1. RECOVERY OF METAL VALUES FROM METALLURGICAL SLAGS” described one of the possible reactions which may take place during the oxidation of the V in Fe-containing slags. The reaction (2) showed the oxidation route for the slag containing $V_2O_5$ and FeO compounds.

Reaction (2) from Chapter 1:

$$2FeO + V_2O_5 + \frac{1}{2}O_2(air) = 2FeVO_4$$

The final product would be a vanadium ferrite (FeVO$_4$), which has some magnetic properties [16] and can be separate by magnetic separation.

But, it is well known fact that vanadium may change its valence depending upon the temperature and partial pressure of oxygen. Therefore the knowledge of the oxidation states of the vanadium in the liquid slag is important. Unfortunately, FactSage did not have a database for the VO$_x$-slag interaction, and therefore, the stability of pure vanadium oxides was used as a guideline to predict the oxidation route of the V-containing slags.

Figure 43 indicates that, at the partial pressure of oxygen equal to $P(O_2)$ in air the $V_2O_5$ is stable below 1650 K. Above 1650 K vanadium changes its valence and VO$_2$ can be formed. Thus, the favourable conditions for the reaction (2) will be air as the oxidizing atmosphere and treating temperature below 1650 K.
From Figure 43, it can also be predicted that by variation of partial pressure of oxygen, the valence of vanadium can be controlled. It means that during the slag oxidation at different partial pressure of oxygen different vanadium ferrites can be obtained, such as FeVO₄, Fe₃V₂O₇, Fe₂V₄O₉ so on... H. Wang et al.[17] studied the oxidation behaviour of Fe-10%V alloy at 1873 K and different (CO₂/O₂) gas mixtures. It was shown, that the main phase presented in the product layer after oxidation was FeV₂O₄. Investigations on the vanadium-iron spinels [18] and their oxidation products during the oxidation of Fe-V solid alloys at P(O₂)=10⁹Pa [19] confirmed the possibility to obtain Fe₂(1-x) V₂xO₃ solid solutions, iron (III) orthovanadate, FeVO₄, V₂O₅ and V₄O₉ with different vanadium contents.

Similarly the oxidation of the chromium containing slags can be described.

From the above reasoning, it can be conclude, that recovery of vanadium in the form of vanadium ferrite from the metallurgical slag is possible by application of the “oxidation concept”. The thermodynamic analyses of the studied slags systems are being currently carried out.
4. SEPARATION METHOD OF THE MAGNETITE/MANGANESE FERRITE PARTICLES FROM LIQUID SLAGS

4.1. Application of the Electromagnetic Buoyancy Force—Cold model studies

The first part of the study consisted of oxidizing the Fe\(^{2+}\) in the liquid slag to Fe\(^{3+}\) and precipitate out the Fe\(_2\)O\(_4\) thus obtained from the slag. While the separation of the magnetite formed by magnetic separation after crushing the cold slag offers a solution, further studies carried out by confocal microscopy at Carnegie Mellon University, USA showed that the precipitated particles (magnetite/manganese ferrite) had extremely fine particle size, of the order of a few microns. The finely dispersed magnetic particles would pose a challenge in the separation process. Hence, as an alternative strategy to magnetic separation of the precipitated magnetite, application of an electromagnetic buoyancy force during the oxidation of Fe\(^{2+}\) in the molten slag can be a feasible solution. In order to verify this, it was necessary to carry out the modelling studies at room temperature.

The steelmaking slag has rather high viscosity (0.3-0.4 Pa*s, data obtained from ThermoSlag software version 1.5 Copyright 2001 by KTH and University of Science and Technology Beijing, China (USTB)) and the precipitated magnetite would be suspended in the liquid slag. The movement of a particle, in general, can be expected to be under laminar-flow conditions. Metallurgical slags have a specific electrical conductivity of 100-120 Sm/m [20], and can act as electrolytes with ionic conductivity. At the temperatures at which the present experiments on the oxidation of liquid slags were conducted, viz. 1723-1773 K, the precipitated magnetite would be paramagnetic (Curie point 845 K). Also, according to Per Kofstad [21] at high temperatures the conductivity of magnetite decreases. Considering this, it was proposed to use non-magnetic particles in the present modelling studies. In order to model the magnetite separation from molten slag, it is necessary to study the movements of both conducting and non-conducting non-magnetic particles which are suspended in a conducting liquid. In the current work, an investigation of the movement of non-conducting, non-magnetic particles in an electrolyte under crossed electrical and magnetic fields was conducted.

It is well known [22, 23, 24], that the rigid-body of a freely suspended particle embedded in a conducting Newtonian fluid can be remotely controlled by externally applied electric and magnetic fields through an electro-magneto-phoretic mechanism. The crossed magnetic and electric fields are used for impurity extraction, species separation, mixing and stirring, and particle manipulation and control [25-31].

46
The EBF acting on a sphere was first introduced by Leenov and Kolin [32] and then modified by Andres [33]. The EBF acting on a sphere ball placed in electrolyte in the crossed electrical and magnetic fields is directly perpendicular to a vector of current density and a vector of the magnetic field (see Figure 44).

Figure 44. A schematic image of the forces, acting on a sphere (dark circle) in the crossed electric and magnetic fields.

Detailed mathematical expressions of the forces acting on the particle in the crossed electric and magnetic fields as well as assumptions involved during the experiment and procedure are presented in Supplement 5 of this thesis.
The experimental setup presented in Figure 45.

Figure 45. A schematic illustration of the experimental setup.

For the present experiments, the materials used were: NaCl-water solution; Ni-electrodes; a plexiglass cavity; plastic spheres of different diameters, and a plexiglass cube, with an rib of 2.1 mm. The average velocity of the sphere under the EBF was measured by a stop watch and a video camera.

The viscosity of electrolyte was measured with the aid of a capillary glass viscosimeter (VPJ-2 GOST 10028-62).

In the present experimental series, more than 200 experiments were carried out. For each value on the plot (see Figure 46), five experiments were employed and average value were plotted (scatter in the values +/- 0.00002). The effects of current density and intensity of a magnetic field on the velocity of non-conducting particle are presented in Figure 46.
4.2. The velocity calculation of crystal magnetite particles under the EBF in practical slag system

When the liquid slag is placed in crossed constant electric and permanent magnetic fields, a complex set of chemical, electrochemical and magnetohydrodynamic phenomena occurs. The metallurgical slag can be represented as an electrolyte with ionic conductivity unless there is variable valency of a particular species, as for example Fe$^{2+}$ and Fe$^{3+}$ [34-38]. Jiao and Themelis [20] have reported that specific electrical
conductivity of steelmaking slags at 1673 K can be calculated using equation (26) and it is in a range of 1.0-1.2 ohm $^{-1}$ cm$^{-1}$ (100-120 Sm/m).

$$\ln(\sigma_f) = -5.21 + 9.92X(FeO) + 5.94(X(CaO)+X(MgO))$$

*equation can be used for slags within the following composition range: $X(Al_2O_3)$ 0-0.03; $X(CaO)$ 0-0.47; $X(FeO)$ 0.1-0.83; $X(MgO)$ 0-0.25; $X(SiO_2)$ 0.17-0.49.

Where $\sigma_f$ - specific electrical conductivity, ohm $^{-1}$ cm$^{-1}$; $X(FeO)$, $X(CaO)$, $X(MgO)$ – mole fractions in the slag.

A direct current flow through a liquid slag liberates heat, which can keep slag in the liquid state:

$$Q = \sigma_f E^2$$

Where $E$ is intensity of an electrical field in a liquid.

By taking typical parameters of slag system (density is 3000 kg/m$^3$, specific electroconductivity of steelmaking slags is 110 Sm/m, dynamic viscosity of the slag is 0.3 kg/m$^3$s), and also by assuming a radius of a magnetite particle to be equal to 0.05 mm, and distance between electrodes 0.1 m, the velocity calculation of magnetite crystal particles under EBF action in real slag system was carried out in a condition, when magnetite would behave as non-conducting particle. Figure 47 shows the dependence of the calculated velocity of the magnetite particles in the real slag system under the EBF influence. As seen from the graphical dependence (Figure 47), the velocity of magnetite is directly proportional to the magnetic field and to the applied potential difference on the electrodes. The velocity rate reaches values of the order of 0.5 mm / min at a potential difference of more than 40 V and a constant value of the magnetic field 1.8 Tesla.

Hypothetically, with future technological development and possible use of supermagnets, in industries, magnetic field up to 10 T can be created and the corresponding particle velocity would increase to 2.5 mm/min (see Figure 47,b).
Figure 47. Dependence on calculated magnetite particle velocity in the particular slag system: a) of potentials on electrodes under magnetic field equal to 1.8 T and b) of intensity of a magnetic field at potentials on electrodes equal to 40B.

Cold modelling in the present work demonstrates the EBF approach provides possible an environmentally-friendly method for the separation of magnetite particles from steelmaking slags. The correlations developed in the present work for the velocity of non-magnetic, non-conductive particles in the electrolyte under EBF can be used as the theoretical basis for semi-industrial and industrial experiments. By using the present results it may be possible to predict the behaviour of particles in a real system with variable parameters such as magnetic field, potential on the electrodes and the particle size.
The optimum parameters for the system can be chosen by industry corresponding to the plant needs. In fact, magnets, which can create magnetic field 1-1.8 T, can be used instead of supermagnets, for electromagnetic separation. Materials for the electrodes can be chosen specific to the melt considered and the solid phase separated at a given temperature. Applied potential on the electrodes will depend on the electrical conductivity of the molten slag.

5. VALUE ADDITION

5.1. Precipitation of nanosize manganese ferrite from the synthetic slags

The spinel-type transition-metal ferrites have obtained increasing interest because of their wide area of technological applications in magnetic recording [39], energy conversion and storage [40], gas sensing [41] and biotechnology [42-44]. To produce the ferrite, nanoparticles were used different methods, as for example, thermal decomposition of organometallic precursors or reduction of metal salts [45]; co-precipitation method; the sol-gel route [46]. All these methods require pure reagents and energy consumption. The present work, on the other hand, shows the feasibility of the nano-manganese ferrite precipitation from the metallurgical wastes (metallurgical slags). The chemical compositions of the synthetic slags used in present studies are shown in Table 7.

Table 7. Chemical compositions of synthetic slags used

<table>
<thead>
<tr>
<th>№</th>
<th>Composition, weight %</th>
<th>Basicity (B)*</th>
<th>FeO/MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>SiO₂</td>
<td>FeO</td>
</tr>
<tr>
<td>1</td>
<td>27.5</td>
<td>27.5</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>33</td>
<td>22</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>37</td>
<td>18</td>
<td>30</td>
</tr>
</tbody>
</table>

* In the present work, basicity, B was defined as: \( B = \frac{CaO}{SiO₂} \).

The furnace arrangement used in the present experiments is presented in Figure 48.
The pre-mixed slag samples in platinum crucibles were placed in an alumina holder and positioned in the even temperature zone of the furnace. The sample was oxidized in air for 30 min and then was cooled down by withdrawing from the hot zone to cold water-cooled end of the furnace. Detailed setup and procedure of the experiment are presented in Supplement 6 of this thesis.

5.1.1. XRD results of the cooled down samples from Horizontal furnaces

The basicity as well as the temperature effect on the manganese ferrite formation was analyzed. The XRD pattern for all the samples showed the presence of manganese ferrite. With increasing basicity (see Figure 49), calcium silicate, as a separate phase, was observed.

In order to investigate a growth trend of manganese ferrite, particle sizes were estimated using the Scherrer formula for the X-Ray particle size determination [47].

\[ L = \frac{k\lambda}{B \cos \frac{x}{2}} \]  

Where \( L \) is the linear dimension of the particle, \( k \) a numerical constant for which Scherrer obtained the value \( 2(\ln 2/\pi)^{0.5} = 0.93 \), \( \lambda \) the wavelength of the incident X-rays (1.54 Å), \( B \) the half-value breadth of the diffracted beam, \( x/2 \) is the Bragg’s angle.
The particle size was found to be dependent on the basicity of the sample. With increasing basicity, the size of the manganese ferrite particles decreased to a nano-scale. With decreasing temperatures, the particle size also decreased. For the basicity equal to two, the calculated manganese ferrite size was approximately 25 nm (see Table 8) in the temperature range 1573K to 1673K.

According to the FactSage 6.1 calculations the main constituent of the Spinel, which would form under present experimental conditions, in the temperature range of 1300K - 1627K would be manganese ferrite. In air at 1627K, only liquid slag can be thermodynamically obtained.

Table 8. Average manganese ferrite size as a function of basicity and temperature.

<table>
<thead>
<tr>
<th>Sample №</th>
<th>Basicity (B)</th>
<th>Experimental temperature,K</th>
<th>Average size, nm (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1673</td>
<td>124.7</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>1673</td>
<td>84.4</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1673</td>
<td>25.5</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1623</td>
<td>24.4</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1573</td>
<td>23.3</td>
</tr>
</tbody>
</table>
The XRD analysis of the samples oxidized at temperatures above 1627K showed the presence of calcium silicate and manganese ferrite. These phases are likely to have been precipitated during cooling of the samples.

5.2. Synthesis of the manganese ferrite from the pure materials and magnetic properties characterization

In chapter 5.1. of this thesis the feasibility of nano-manganese ferrite precipitation from metallurgical wastes (metallurgical slags) was demonstrated. In order to get an understanding of the magnetic properties of the manganese ferrite recovered from slag treatment, it was necessary to synthesize a reference compound from pure precursors. The MnFe$_2$O$_4$ nanopowder was synthesized by the oxalate route. The details of the synthesis and characterization of the product presented in Supplement 7 of this Thesis. The products after the synthesis were analyzed by XRD and SEM techniques.

The XRD patterns indicated the formation of manganese ferrite. The obtained particle size was in the range of approximately 25-30 nm. The magnetic properties measured at 300 K were: saturation magnetisation (Ms); remaining magnetization (Mr); and coercivity (Hc). Obtained nano- MnFe$_2$O$_4$ was a soft ferromagnet. The field dependence of the magnetization at 300 K shows 6.44 emu/g remanence (Mr) for the 25 nm particles, which slightly increases to 6.90 emu/g for the 30 nm particles. The saturation magnetization (Ms) increases with increasing particle size and decreasing coercivity (Hc). The Ms values at room temperature is lower than the bulk (80 emu/g [48]). The reduced saturation magnetization of manganese ferrite particles was also found by other authors [48-49] and was explained by a magnetic dead layer on the surface of particles.

The present experimental results are compared with earlier works by Chen and Muroi reported in literature in Figure 50. Chen prepared fine manganese ferrite particles in the size range 5-15 nm by an aqueous phase co-precipitation method. Muroi investigated the size-dependent magnetic properties of ultrafine MnFe$_2$O$_4$ powders (9.5-40 nm) synthesized by mechanochemical processing. From Figure 50, it can be seen that obtained results are in agreement with literature data.
Figure 50. Saturation magnetization (Ms) as a function of inversed particle size (D).

The present results can be used as a guide line for the magnetic properties characterization of the manganese ferrites obtained from metallurgical slags. As was mentioned in earlier, the investigations by on manganese ferrite precipitation from metallurgical slags showed the possibility to obtain MnFe$_2$O$_4$ particles in the size of 25 nm. The present results show that the magnetic property of manganese ferrite is independent of the synthesis route adopted. The nano-manganese ferrite obtained from metallurgical slags is also likely to be a soft ferromagnet, with 43.96 emu/g saturation magnetization, 147.97 Oe coercivity and 6.44 emu/g remanence.

6. INDUSTRIAL IMPORTANCE OF THE PRESENT RESULTS

6.1. Environmental impact

In EU in 2007 the total level of steel production was ≈210Mt and in the world ≈1344 Mt. In EU, steel production in bottom oxygen furnace (BOF) was 59.6% and in electric arc furnace (EAF) 40.25 %. In the world, the production of the steel was 66.35% and 31.2% in BOF and EAF respectively [50].

The slag yield in steelmaking reaches 100-110 kg/t of steel [51-52]. This means that in 2007, 21 Mt of slag were generated in EU and 134 Mt of slag in the world. Significant amount of the slag (40 %) remain in the dumps, damaging the environment and requiring a land for storage [2, 3].

The increasing world’s demand for metallurgical products is thus the cause of formation of an increasing volume of slag, which forces searching for various methods of its utilization.
The present author had proposed a new strategy to recycle the metallurgical slag. The concept was based on oxidation of bivalent iron to trivalent form with further magnetic separation.

In the world practice, most of the currently existing process solutions are aimed to reduce the iron oxides to metallic iron [53]. This would increase the energy needs of the process and require suitable reductants. For example, carbon is a natural choice as a reductant. The corresponding chemical reactions can be written as:

\[
\text{FeO} + \text{C} = \text{Fe} + \text{CO} \quad (29)
\]

\[
2\text{FeO} + \text{C} = 2\text{Fe} + \text{CO}_2 \quad (30)
\]

The CO/CO\(_2\) gas produced has a strong detrimental effect on the environment. Proposed method of slag utilization using an oxidation route is environmentally friendly method. After oxidation of the slag in air, final products are calcium silicates and magnetic materials, which can be separated by magnetic separation. During this process there are no damaging gasses or components can be created. This makes proposed method more advanced compared to existing solutions.

The oxidation method can be applied to the new produced slags as well as to the dumped slags. This allows decreasing the area used for saving slags, and open new land for new construction.

### 6.2. Economic impact

The major solid waste product of the steelmaking industry is slag and its main constituents are: CaO, SiO\(_2\), Al\(_2\)O\(_3\), MnO, FeO and others. Average chemical composition of the steelmaking slag is presented in the Table 9.

Table 9. Average chemical composition of the steelmaking slag, w%.

<table>
<thead>
<tr>
<th>FeO</th>
<th>SiO(_2)</th>
<th>CaO</th>
<th>MgO</th>
<th>Al(_2)O(_3)</th>
<th>MnO</th>
<th>P(_2)O(_5)</th>
<th>Cr(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-39</td>
<td>10-14</td>
<td>22-37</td>
<td>5-10</td>
<td>2-3.7</td>
<td>4-6.5</td>
<td>0.5-0.85</td>
<td>0.7-2.3</td>
</tr>
</tbody>
</table>

The slag contains 17-39 % of FeO and 22-37 % of CaO and is therefore very valuable material. For example, in 2007 in EU, the yearly volume of the steelmaking slag contained up to 8.2 Mt of iron in the form of oxides (non-magnetic part) and up to 7.8 Mt of lime. These volumes correspond to around 41Mt of medium grade iron ore and 16 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. By analogy, calculations were carried out for the world slag production and presented in Table 10.

Table 10. Economical advantages of the “oxidation concept” of the slag utilization.

<table>
<thead>
<tr>
<th>Amounts of the constituencies of the slag generated per year.</th>
<th>Volume of the materials, which can be saved/produced per year by application of the “oxidation concept”.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO_{Slag} w%/Mt  CaO_{Slag} w%/Mt  MnO_{Slag} w%/Mt</td>
<td>Medium grade iron ore, Mt  Limestone, Mt  Manganese ferrite, Mt</td>
</tr>
<tr>
<td>EU  39/8.2  37/7.8  6.5/1.4</td>
<td>41.0  16.0  4.5</td>
</tr>
<tr>
<td>World  39/52.3  37/49.6  6.5/8.7</td>
<td>261.3  99.0  28</td>
</tr>
</tbody>
</table>

The slags contain also 4–6.5 % MnO from which, during oxidation of the slag 4.5 Mt of manganese ferrite can be produced in EU and up to 28 Mt in the world per year (see Table 10).

Thus, applying an “oxidation concept” for the recycling of the metallurgical slag, 261.3 Mt of medium grade iron ore and 99 Mt of limestone can be saved, and/or 28 Mt of manganese ferrite can be produced in the world per year.
SUMMARY

In the current work, the oxidation of FeO in silicate slag was investigated for the purpose of recovery through magnetic separation. For the experiments, synthetic slags of the ternary FeO-CaO-SiO$_2$ and quaternary FeO-CaO-SiO$_2$-MnO systems were chosen. The mechanism of oxidation of FeO in molten slags was analyzed by combining advantages of Confocal Scanning Laser Microscopy and Thermogravimetric technique.

The TGA experiments of the ternary slag systems showed that, during 10-15 min, 70-90% of oxidation was achieved. Increase of temperature in the range 1623K-1723 K was found to cause an increase in the rate of the reaction. The oxidation rate was found to increase with increasing basicity and % FeO in the system. A linear correlation was found between the thermodynamic activity of FeO and the degree of oxidation.

A thermogravimetric analysis for the quaternary slag system showed that, increase of the temperature in the range 1500K-1600K was found to cause an increase in the rate of the reaction. XRD analyzes of the samples after oxidation showed the presence of manganese ferrite, magnetite and calcium silicate. The phase characterization of the spinel formed at different temperatures was explained on the basis of thermodynamic calculations. The basicity effect on the spinel formation during oxidation of liquid FeO-CaO-SiO$_2$-MnO slag was discussed.

The thermograms for oxidation showed an initial incubation period corresponding to the oxygen dissolution in the slag followed by a chemical reaction-controlled stage. At later stages, the reaction rate was controlled by diffusion. The mechanism of the oxidation process was described by means of a theoretical model and excellent agreement with the experimental results could be achieved.

Kinetics of the crystal precipitation from the liquid FeO-CaO-SiO$_2$ and FeO-CaO-SiO$_2$-MnO slags has been investigated by Confocal Scanning Laser Microscopy. Successive CSLM images showed the crystal formation during oxidation. With time, the crystals grew and agglomerated, reaching, in some cases, 50 µm in length. Different shapes of crystals were observed at different temperatures. The SEM-EDS results showed the presence of calcium silicate and spinel containing manganese ferrite and magnetite. The phase characterization of the spinel formed at different temperatures was explained on the basis of thermodynamic calculations.
A Time-Temperature-Transformation diagram was constructed based on CSLM results. Corresponding mechanism of the crystal precipitation during oxidation could be expressed by a balance of the gas-phase mass transport and liquid state diffusion of the mobile species, which counteract with one another over the temperature.

The precipitation of nano-manganese ferrite from the FeO-CaO-SiO$_2$-MnO slag system during oxidation was investigated. The manganese ferrite particle size was calculated using the Scherrer formula. With increasing basicity of the sample, the particle size of manganese ferrite was decreased. At basicity equal to 2, the manganese ferrite particle size was determined to be approximately 25 nm. The MnFe$_2$O$_4$ nanopowder was synthesized by the oxalate route. The obtained particle size was in the range of approximately 25-30 nm. The magnetic properties measured at 300K were: saturation magnetisation (Ms); remaining magnetization (Mr); and coercivity (Hc). The particle size effect on the magnetic properties of MnFe$_2$O$_4$ was in agreement with the trend reported in literature.

The Cold model studies were performed to study the potential way of the magnetite particles separation from liquid slags. The effect of current density, magnetic field, radius, and the shape of the particle on the particle velocity were analysed. With increasing applied current density, magnetic field and radius of the particle, velocity of the particle was increased. Theoretical application of the obtained data on the real magnetite particle/liquid slag system showed that the magnetite will have a subcritical behaviour, and will move with approximate velocity of 0.1-2.5 mm/min.
FUTURE WORK

In the present work author showed the economical and the same time environmentally friendly solution to recover iron/manganese in the form of magnetite/manganese ferrite from metallurgical slags. The laboratory experiments on the synthetic ternary FeO-CaO-SiO$_2$ and quaternary FeO-CaO-SiO$_2$-MnO slags systems were successful. As the next step the trial experiments on the metallurgical plant are needed.

Furthermore the investigations of the nano-manganese ferrite formations from the MnO-, and FeO- containing slags needs to be continued. The magnetic properties of the synthesized nano-manganses ferrite need to be characterized.

Kinetic and thermodynamic investigations of the V- and Cr- containing slags are required. The possibility of vanadium and chromium ferrite precipitation during slag oxidation should be studied. The basicity and temperature effects on the ferrite formation should be analyzed.

Further investigations of the application of electromagnetic buoyancy force during the particle separation from the liquid slags needs to be carried out. The details of the experimental conditions for the semi industrial and industrial trial should be settled.
REFERENCES


[50] www.worldsteel.org


