Energy and environmental optimization of some aspects of EAF practice with novel process solutions

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Doctoral Thesis

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Abstract

The objective of the present thesis is to optimize the electric arc furnace (EAF) practice from an environmental viewpoint. Two aspects that meet the requirements of the secondary steelmaking industries today, viz. Mo alloying with maximum retainment of the alloying element in molten steel and optimization of foaming by carbonate addition with a view to optimize the energy need of the process. Both these aspects would also have a significant impact on the process economy.

Iron molybdate (Fe$_2$MoO$_4$) has been synthesized from commercial grade materials and proposed as a new potential precursor for steel alloying with Mo. The thermal stabilities of different molybdates, viz. Fe$_2$MoO$_4$, CaMoO$_4$ and MgMoO$_4$, were studied using thermogravimetry analysis (TGA). It was found that Fe$_2$MoO$_4$ is the most stable one and doesn’t evaporate in Ar atmosphere when heating up to 1573 K.

The synthesis of Fe$_2$MoO$_4$ requires high temperature (1373 K) and long holding time (up to 16 hours). In a view of this, the possibilities for in-situ formation of Fe$_2$MoO$_4$ and CaMoO$_4$ from their precursor mixtures were studied with the aid of high-temperature X-ray diffraction (XRD) and TGA analysis. Laboratory and industrial trials on steel alloying with Mo were conducted using precursor mixtures as sources of Mo. It was found that the mixture, which contains FeO$_x$, MoO$_3$ and C (Fe$_2$MoO$_4$ precursor), can provide the Mo yield up to 98 % at both the laboratory as well as industrial trials. The Mo yields even in the case of C+MoO$_3$ and C+MoO$_3$+CaO mixtures were around 93 % in these trials. The higher yield for the MoO$_3$+C+FeO$_x$ mixture was attributed to the stabilization of Mo in the precursor (marked by the decrease in the Gibbs energy of Mo) and the readiness to dissolve in the steel bath.

The heat effect of the slag foaming with carbonates addition was studied at 1623 and 1673 K with the aid of thermal analysis technique with a new crucible design. Experiments were conducted by adding limestone and dolomite pieces of defined shapes (together with iron sinkers) in molten slag and monitoring the temperature changes accompanying the decomposition of carbonates. It was found that the decomposition energies for dolomite and limestone for the studied slag composition are in the range 56-79 % of theoretical values,
which is linked to the energy saving effect of slag foaming. No influence of sample shape on decomposition energy was found both for limestone and dolomite. The kinetics of slag foaming by limestone particles was studied at 1773 K with the aid of X-ray imaging system. A model was proposed to describe the decrease in foam height with time on the basis of CaO shell formation during decomposition reaction. The energy impact of limestone and raw dolomite addition was examined in a 100-ton EAF. It was found that, in the case of addition of carbonates after the scrap is completely molten; the endothermic heat effects for limestone and dolomite (2255 and 2264 kJ/kg respectively) were only 70 % from theoretical values. This is indicative of the resistance to heat transfer due to increased foaming.

**Keywords:** Fe$_2$MoO$_4$ synthesis, CaMoO$_4$ formation, steel alloying, Mo yield, industrial test, molybdates stabilities, MoO$_3$ evaporation, slag foaming, limestone decomposition, EAF, energy saving, thermal analysis, raw dolomite; high temperature XRD.
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Supplements

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Supplement 1: MoO₃ evaporation studies from binary systems towards choice of Mo precursors in EAF
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Supplement 2: Synthesis and characterization of Fe₂MoO₄ as a precursor material for Mo alloying in steel
A. Chychko, L. Teng, M. Nzotta and S. Seetharaman
Steel Research international, Sent for publication in July 2010

Supplement 3: Fe₂MoO₄ as a precursor material for Mo alloying in steel (Part II): Up-scaling test
A. Chychko, L. Teng, M. Nzotta and S. Seetharaman
Steel Research international, Sent for publication in July 2010

Supplement 4: Foaming in Electric Arc Furnace Part I: Laboratory Studies of Enthalpy changes of Carbonate Additions to Slag Melts
A. Chychko and S. Seetharaman
Metallurgical and Materials Transactions B, Sent for publication in March 2010

Supplement 5: Foaming in Electric Arc Furnace Part II: Foaming visualization and Comparison with Plant trials
A. Chychko, L. Teng, and S. Seetharaman
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Supplement 6: Process for making a steel melt containing carbide forming elements from iron based raw material and a mineral containing the carbide forming element, an alloy mixture and use of a mineral containing L. Teng, M. Nzotta, S. Seetharaman, A. Chychko, J.-O. Andersson Patent application № 1050721-8 received on 01.07.2010

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A. Chychko and S. Seetharaman
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Energy Saving effect of slag foaming by carbonate additions in EAF Process
A. Chychko, L. Teng, and S. Seetharaman
Workshop on utilization of steelmaking slags with by-product recovery
Krakow, Poland, 10-11th May 2010

The determination of the total heat effect of slag foaming in an EAF
A. Chychko and S. Seetharaman
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Supplement 1: Literature survey, experimental work, data analysis, major part of the writing
Supplement 2: Literature survey, experimental work, data analysis, major part of the writing
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Supplement 4: Literature survey, experimental work, data analysis, major part of the writing
Supplement 5: Literature survey, experimental work, data analysis, major part of the writing
Supplement 6: Experimental work, data analysis
**Contents**

Abstract .............................................................................................................................. I  
Acknowledgements ........................................................................................................... III  
Supplements....................................................................................................................... V  
1. Introduction ...................................................................................................................... 1  
   1.1 Mo addition .............................................................................................................. 2  
   1.2 Slag foaming .......................................................................................................... 3  
2. Background of the study .................................................................................................. 4  
   2.1 Fundamental aspects of steel alloying with Mo ....................................................... 4  
      2.1.1. Criteria for choosing alternate Mo sources, advantages and disadvantages ....... 4  
      2.1.2. The evaporation of MoO$_3$ from different alloying sources of Mo ................. 5  
   2.2. Slag foaming practice in an electric arc furnace (EAF) ........................................... 7  
      2.2.1. Chemical reactions leading to slag foaming in EAF ......................................... 7  
      2.2.2. The influence of the slag foaming on the EAF efficiency .................................. 8  
   2.3. Strategy and objectives in the present thesis ......................................................... 8  
3. Experimental work ......................................................................................................... 11  
   3.1 Thermogravimetry (TGA) ........................................................................................ 11  
   3.2 Gas chromatography (GC) ....................................................................................... 13  
   3.3 High-temperature X-Ray diffraction (XRD) ............................................................ 14  
   3.4 Steel alloying experiments ....................................................................................... 14  
      3.4.1. Small scale experiments in laboratory ............................................................... 14  
      3.4.2. Industrial trials ................................................................................................. 17  
   3.5. Heat effect of slag foaming measurements ............................................................. 18  
   3.6. X-Ray radiography system .................................................................................... 21  
   3.7. Plant trials on slag foaming ................................................................................... 22  
4. Results and discussion .................................................................................................... 24  
   4.1. The development of new precursor for steel alloying with Mo ............................. 24
4.1.1. CaMoO₄, MgMoO₄ and Fe₂MoO₄ stabilities with respect to evaporation and oxidation .................................................................................................................. 24

4.1.2. The possibilities of CaMoO₄, MgMoO₄ and Fe₂MoO₄ in-situ formation from industrial grade materials .................................................................................................................. 25

4.1.3. The investigation of CaMoO₄ and Fe₂MoO₄ precursors reduction processes ...... 29

4.1.4. Laboratory trials on steel alloying from 16-g- to 500-g-scale experiments ........ 32

4.1.5. Industrial trials on steel alloying in 3 ton induction furnace ........................ 34

4.2. Slag foaming caused by carbonates decomposition ................................................. 36

4.2.1. Thermodynamic modeling results ........................................................................ 36

4.2.2. Measured energies of decomposition for natural limestone and dolomite ........ 37

4.2.3. Plant data analysis ................................................................................................ 42

4.2.4. Studies on the kinetics of slag foaming and modeling of the foam height changes .................................................................................................................. 44

5. Summary and conclusions .......................................................................................... 49

6. Future work ................................................................................................................. 51

References ..................................................................................................................... 52
1. Introduction

Metallurgy is an important part of modern engineering science, which provides the mankind with metals which are materials with unique properties. The appearance of steelmaking initiated a huge acceleration in the development of our civilization. Ferrous metallurgy is one of the most energy- and resource consuming part of the industry. In recent times, many ecological problems are traced to this voluminous industry with huge production of different steel grades. This necessitates improvement and even redesigning of traditional technologies, marking a “revolution” in steelmaking.

This work was carried out as a part of the national project of Eso-Steel production, in which the Division of Materials Process Science is an active participant with the objective, “Retention, recovery and recycling of valuable metals”. The project aims at tailoring the existing processes and come up with new process solutions for an optimization of the steel production towards a better environment. The recovery and reutilization of valuable metals for steel alloying, \( \text{viz.} \) Mo, Cr, V, Mn and even Fe in steelmaking routes is the main goal. The process concepts would be based on thermodynamic and kinetic considerations of high-temperature processes. The Eco-steel production concept, aims at the maximum utilization of waste materials and byproducts (secondary resources) into steel production cycle and subsequent lowering in the consumption of natural resources and nature pollution.

The present work deals with electric arc furnace (EAF) process optimization towards energy and material saving by suitable modifications of the current technology. The criteria for these solutions are easiness of implementation, as well as resource- or energy efficiency improvements.

The research work on which the present dissertation is based consists of two big parts. The first part focuses on the studies for Mo yield improvement. And the second part focuses on slag foaming benefits, arising from direct addition of limestone or dolomite to an EAF. The strategy diagram of the thesis work is presented in Figure 1.1. As mentioned earlier, the prime aim is to achieve a more efficient and ecological usage of resources during EAF steel production. Such efficiency arises from the direct utilization of natural or waste materials in the EAF process. For example, in the production of tool steel, Mo addition is carried out by choosing suitable precursors which enable an elimination of the prior production of ferromolybdenum alloy. Similarly, adjusting the basicity is carried out using limestone instead of CaO eliminating the calcination step.
Different molybdenum sources are known to be used in tooling steel production. The most common one is the ferromolybdenum alloy, which is usually added during steel composition adjustment in a ladle treatment. This material possesses high density and easily dissolves in steel. As a result, a very high yield of molybdenum in steel can be achieved. The major disadvantage of this material is its relatively high production cost. In view of this, alternative molybdenum raw materials have been used for steel alloying. The cheapest one is the natural molybdenum trioxide (MoO\textsubscript{3}), which is available in the form of the mineral molybdite. The main drawback for the direct molybdenum trioxide addition in EAF is the evaporation of MoO\textsubscript{3}, which has a high vapor pressure at steelmaking temperatures. In the case of the EAF practice at Uddeholms AB, Hagfors, Sweden, the losses of molybdenum to the furnace exhaust dust can reach up to 7 %. This will create not only valuable element loss, but also ecological problems as Mo is a heavy metal and is likely to end up in the biosphere. One of the solutions to this problem can be the conversion of MoO\textsubscript{3} into more stable molybdates like CaMoO\textsubscript{4}, MgMoO\textsubscript{4} or Fe\textsubscript{2}MoO\textsubscript{4}. It is to be noted that it is not economically attractive to synthesize any compound before addition to steel melts, as this involves additional costs due to extra unit processes. Thus, \textit{in situ} formation of the molybdates during scrap melting would be highly desirable. Further, the raw materials should be inexpensive, recyclable industrial wastes. In the present work, investigations were carried out in order to find out
suitable Mo compound, formed from commercial ingredients as an economically viable alternative for Mo addition to steel melts in the EAF.

1.2 Slag foaming

The beneficial effects of slag foaming in EAF practice are well-known. They include, for example: thermal insulation of the arc and steel surface, noise reduction, metal protection from nitrogen dissolution etc.

Slag foaming has been studied systematically for more than 50 years since Cooper and Kitchener introduced a new theory of slag foam stability [1-2]. During the past 20 years, a great deal of attention has been paid to foam stability investigations, an important milestone being the concept of slag foaming index [3], in view of the importance in EAF steelmaking.

In the EAF process, thermal insulation of the arc by slag foam plays a key role in process efficiency. Traditionally, slag is foamed by carbon injection into liquid steel-slag interface. The process is well-known and has been studied for many years. Alternative way for foam creation can be direct addition of carbonates, for example limestone or dolomite. This way can offer some benefits, such as better reaction control, the possibilities to create good foam even during stainless steel making, and the utilization of CO\(_2\) as additional deoxidizer.

However, it can be concluded from the literature survey, that the slag foaming with carbonates is not usual in steelmaking practice. It is traditionally believed that such reactions (which are endothermic) are not favorable for energy balance of the total process since they require additional heat for the decomposition process. However, there is no available data on heat balance for slag foaming by carbonates decomposition. On the other hand, if the process of lime production can be considered as a part of steelmaking route, it is clear that limestone calcination in a separate furnace will require the same amount of energy but without possible additional benefits, like slag foaming or CO\(_2\) utilization. Thus, direct addition of carbonates to EAF could offer an interesting alternative.

In the present work, an attempt was made to study the energy effect of slag foaming caused by carbonates decomposition both in laboratory scale and application of the same to industrial scale. The investigations of slag foaming include several parts: the major one describes the laboratory experiments where the thermal effects are measured and modeled (Supplement 4). Separate parts deal with X-ray visualization studies of carbonate-based foaming and analysis of the results from industrial EAF practice, where the advantages of foaming by carbonate addition are evaluated (Supplement 5).
2. Background of the study

2.1 Fundamental aspects of steel alloying with Mo

2.1.1. Criteria for choosing alternate Mo sources, advantages and disadvantages

At least two factors should be considered to improve the yield of Mo. First, the substance has to be stable at high temperatures to avoid fast evaporation of Mo in the form of any gaseous spices. Another important criterion for the choice of Mo-precursor should be the easiness of dissolution in steel melt. A very stable compound is likely to float on the steel surface and can get assimilated in the slag phase instead of reacting with steel, thus lowering the yield of Mo in the steel bath. The first criterion can be evaluated on the base of thermodynamic data on substances stabilities, while the second one involves kinetics and requires experimental investigations.

It is known that MoO$_2$ has much lower equilibrium partial pressure than that of MoO$_3$ even at high temperatures [4]. Hence, reduction of MoO$_3$ to MoO$_2$ could minimize the loss of Mo to the vapor phase. MoO$_2$ can be further stabilized in the condensed phase by lowering the Gibbs energy through the formation of a stable compound. In the present work, investigations were carried out in order to examine the suitability of Fe$_2$MoO$_4$, formed from commercial ingredients as an economically viable alternative for Mo addition to steel melts in the EAF.

According to Fe-Mo-O ternary phase diagram at 1273 K [5], Fe and Mo form two ternary oxides, viz. 2FeO-MoO$_2$ (Fe$_2$MoO$_4$) and 2FeO-MoO$_2$ (Fe$_2$Mo$_3$O$_8$). In the present context, the thermodynamic stabilities of both these compounds are considered as both can be potential molybdenum precursors. The formation of these oxides can be described by the equations:

\begin{equation}
2\text{FeO}(s) + \text{MoO}_2(s) = \text{Fe}_2\text{MoO}_4(s) \tag{2.1}
\end{equation}

\begin{equation}
2\text{FeO}(s) + 3\text{MoO}_2(s) = \text{Fe}_2\text{Mo}_3\text{O}_8(s) \tag{2.2}
\end{equation}

The Gibbs energies of formation the various Mo compounds and the oxides of carbon (which are relevant for the reduction reactions) per one mole of O$_2$, as functions of temperature up to 1500 K, as retrieved from Thermocalc SGTE Solutions database v.4 are presented in Figure 2.1. The data on the Gibbs energies of formation of Fe$_2$Mo$_3$O$_8$ and Fe$_2$MoO$_4$ were taken from [6].
It is seen that the Fe-Mo ternary oxides have lower Gibbs energies compared to pure MoO$_2$, thus exhibiting higher stabilities. Besides higher stabilities, they can be prepared from industrially available waste and natural materials. Fe$_2$MoO$_4$ can be proposed as the most attractive substance, because the higher ratio of FeO to MoO$_2$ should lower the activity of the latter oxide and thus stabilize Mo.

2.1.2. The evaporation of MoO$_3$ from different alloying sources of Mo

As mentioned earlier, Mo “stabilization” (reduction in the vapour pressure of Mo as trioxide) can be achieved by the formation of more stable molybdates from MoO$_3$. Natural molybdenum oxide (MoO$_3$) is the cheapest source of Mo. However, to improve Mo yield in the steel melt, the evaporation rate of MoO$_3$ has to be lowered. The evaporation of molybdenum trioxide, has been studied for the past 50 years in connection with the purification of MoO$_3$ [7], ferromolybdenum alloy production [8], performance of Mo-containing materials at high temperatures [9] and designing of catalysts [10-11]. It was found that pure MoO$_3$ sublimes above 973 K, but the evaporation rate becomes very significant beyond the melting point of MoO$_3$ at 1068 K [9]. It was also found in [7] that many metal oxides retard MoO$_3$ evaporation even at small concentrations and the evaporation rate should be inversely proportional to the ratio (stabilizing oxide / MoO$_3$). One exception is Al$_2$O$_3$ which is not reported to have any noticeable influence on MoO$_3$ evaporation rate [12]. Alkaline-earth molybdates can form alternative precursors for Mo for
steel alloying [4]. Magnesium and calcium molybdates can easily be prepared by the sintering of MoO$_3$ with appropriate oxides at temperatures higher than 873 K [13].

The thermodynamic calculations were performed to analyze the relevant stabilities of different molybdates toward MoO$_3$ evaporation. Only cheap oxides were considered during such analysis. The following reactions describe MoO$_3$ losses from the substances:

\[
\begin{align*}
\text{CaMoO}_4(s) &= \text{CaO} + \text{MoO}_3(g) \quad (2.3) \\
\text{MgMoO}_4(s) &= \text{MgO} + \text{MoO}_3(g) \quad (2.4) \\
\text{FeMoO}_4(s) &= \text{FeO} + \text{MoO}_3(g) \quad (2.5)
\end{align*}
\]

The results of Gibbs energy of decomposition calculations are presented at Figure 2.2.

![Figure 2.2 – Calculated standard Gibbs energy changes of the molybdates decomposition as a function of temperature: 1-CaMoO$_4$; 2-MgMoO$_4$; 3-FeMoO$_4$](image)

It can be concluded that CaMoO$_4$ possesses the highest stability and consequently, low MoO$_3$ vapour pressure. On this basis, it can be concluded that Fe$_2$MoO$_4$, CaMoO$_4$ and MgMoO$_4$ possess the highest stabilities toward Mo species evaporation and can be chosen as alternative Mo sources for steel alloying. Investigations carried out on the evaporation of MoO$_3$ from alkali-earth molybdates by Kazenas [14] showed that many molybdates evaporate as a mixture of initial salt and MoO$_3$ derivatives, which requires experimental investigations of the evaporation rates. An important requirement for a good precursor for Mo addition to steel melts is the dissolution rate of the precursor should be fast. The higher stability of the compound may lead to a lower dissolution rate of Mo in the steel leading to “floating” of the compound on the surface, leading to lower Mo yields. Thus, many factors can affect the
yield of Mo during steel alloying and the further experimental investigations are required to choose the most suitable Mo precursor.

2.2. Slag foaming practice in an electric arc furnace (EAF)

2.2.1. Chemical reactions leading to slag foaming in EAF

There are two types of reactions which can be used for slag foaming. The most familiar one is the carbon oxidation by oxygen dissolved in the metal:

\[ [C] + [O] = \{CO\} \]  \hspace{1cm} (2.6)

This reaction is exothermic and sometimes is difficult to control. For example, it can cause too vigorous foaming in oxygen-blowing furnaces. This reaction has been studied for many years and will not be considered in the present work.

Another type of slag foaming reactions is the decomposition of carbonates or other substances, which can produce gases at high temperature:

\[ \text{CaCO}_3(s) = (\text{CaO}) + \{\text{CO}_2\} \]  \hspace{1cm} (2.7)

\[ \text{CaCO}_3\cdot\text{MgCO}_3(s) = (\text{CaO}) + (\text{MgO}) + 2\{\text{CO}_2\} \]  \hspace{1cm} (2.8)

This kind of foaming does not require extra O\textsubscript{2} and C addition and could be used in ultra low carbon or stainless steel production. Various foaming agents like calcium carbonate and nitrate were studied toward gas generation. [15]. These reactions do not have resident time because they are limited only by heat transfer to the system (these reactions are generally endothermic), which is usually much faster than mass transfer. The detailed study of the kinetics of slag foam height caused by marble sphere decomposition in borate melts at 1196 K was carried out by Chu and colleagues [16]. It was found that small-sized granules make higher foaming layer; but foam life was shorter, while large-sized granules make thinner foam layer but longer foam life time. These authors also found that, in the case of slag foaming by limestone, there is an influence of slag composition on decomposition kinetics. It was attributed to the dissolution rate of CaO shell, formed during CaCO\textsubscript{3} decomposition. Further, when the CaO porous shell was thicker, the bubble size of CO\textsubscript{2} released was smaller, which should also affect the foam stability. Comparing the decomposition of limestone and dolomite in Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7}-CaO-MgO melts at 1173 K, Niu \textit{et al.} found that same size dolomite sphere provided slightly longer foam life than one from limestone [17]. The difference was explained by the different crystal structure of minerals.
2.2.2. The influence of the slag foaming on the EAF efficiency

It is to be noted that foam creation requires an additional heat for both decomposition reaction and heating of the gaseous products. On the other hand, well-foamed slag should improve the efficiency of EAF process. The electric arc plasma has a temperature from 5000 to 20 000 K [18], and it is obvious that the good insulation of the arc by slag foam plays a key role in process efficiency. According to Fedina et al [19], if only half of the electric arc length is in the slag, the part of energy, which is transferred from the arc to the liquid metal will be only 31-42 %. However, if the arc is totally immersed into the slag, the metal bath will receive 50 % of the arc power and consequently, the coefficient of energy usage will increase from 52-66 to 80-93 %. The same authors have also been reported that, in the case of higher slag foam, the efficiency of the CO post-combustion also increases. At the same time, the input power can also be increased because of higher arc stability, which results in the decrease of the whole heat duration and consequent heat losses. Finally, the energy saving effect of 10-30 kWh/ton was reported in the case of well-controlled slag foaming for 150 ton electric arc furnace. Fruehan suggests that energy transfer efficiency improves from 40% without a foaming slag to 60-90 % efficiency when the slag is foamed [20]. Richard et al. [21] developed a model to describe the melting process and chemical reactions in an EAF depending on reagents and energy additions. The energy model considers the radiation and convective heat transfer, taking place between different zones, the furnace components, and the arc. They assumed, using available data, that if the arc is fully covered by the foaming slag, almost 70% of the arc energy will be blocked from reaching the wall and instead transported to the steel. This is especially important for oxygen refining period when there is no solid scrap around the arc. Authors [22] reported that in an EAF around 18 % of the energy from the arc is delivered directly to the steel, 2 % is absorbed by the electrode, and 80 % is scattered around in the form of radiation. The calculated radiation intensity from the arc is decreased from 10 to 3.5 MW/m² within the double radius of each electrode (600 mm) in the center of the bath, and to 0.125 MW/m² at the furnace wall.

It can be concluded from the literature survey, that there are no systematic results on the influence of slag foaming processes on the total energy balance of EAF.

2.3. Strategy and objectives in the present thesis

The first part of the current PhD project aimed for the creation of the cheap alternative source for steel alloying with Mo. To achieve the aim, the reasons of the poor yield from mineral concentrate of MoO₃ were analyzed and thermodynamic modeling was performed in
order to choose more suitable precursors of Mo. Two main criteria were considered during the thermodynamic analysis: 1) the vapor pressure of MoO$_3$ as a function of temperature; 2) the thermodynamic stability of a substance. The selection of the raw materials was limited to waste and cheap sources of other elements, which could be used for the preparation of more suitable precursors for steel alloying with Mo.

After choosing the most suitable molybdates as candidates for Mo sources, more detailed thermogravimetry investigations were performed on the molybdates thermal stability to confirm the results of thermodynamic analysis.

During the next stage, it was interesting to achieve *in-situ* formation of Fe$_2$MoO$_4$ and other molybdates when mixing initial components and heat them together during scrap melting. It was also attractive in a view of cost lowering, as it can simplify the process of alloying material production and combine it together with EAF practice. To study the possibilities for *in-situ* formation of CaMoO$_4$, MgMoO$_4$ and Fe$_2$MoO$_4$ from their precursor mixtures, a number of methods were used, such as thermogravimetry (TGA), gas chromatograph (GC), high-temperature X-ray diffraction (HT-XRD) and laboratory trials on steel alloying.

With the knowledge obtained from these studies, laboratory experiments of Mo-addition were performed in a small induction furnace in 16-g-scale. It was found that, among the molybdates studied, Fe$_2$MoO$_4$ provided the highest yield. The materials with the most promising characteristics were tested in a larger scale laboratory and, finally, in industrial scale experiments and compared with MoO$_3$ as a reference material. The sequence of investigation, all the methods used and material tested are shown in the Figure 2.3.

The second part of the thesis is devoted to slag foaming investigations. To the author’s knowledge there was no experimental technique to measure the total heat balance of slag foaming process. Therefore, the design and validation of such a technique became the most important part in the slag foaming work. Besides the technique, the kinetic studies of slag foaming and industrial data analysis were performed in order to confirm the observations from the laboratory studies. The research plan and instruments for the investigation on heat balance of slag foaming are shown in Figure 2.4.
Figure 2.3 – Research plan and instruments for a new Mo source development

Figure 2.4 – Research plan and instruments for the investigation on heat balance of slag foaming
3. Experimental work

Materials. Pure iron powder (less than 200 mesh, 99 %), C (mold graphite powder, 99.9 %, < 0.5 mm), MoO₃ (99+ %), MoO₂ (99 %), Fe₂O₃ (97+ %), CaMoO₄ (99.8 %), MgMoO₄ (99.9 %), CaO (99.9 %) and MgO (99+ %) were supplied from Alfa Aesar company. Fe₂O₃ was preheated at 473 K for 4-6 hours to remove residual H₂O, while CaO and MgO powders were preheated at 1073 K for 24 hours to remove residual H₂O and CO₂. Ar gas (purity 99.999 %), CO and technical air were supplied by AGA gas company, Stockholm. Fe₂MoO₄ used in the present work as reference material was synthesized from a mixture of (Fe₂O₃+Fe+MoO₃) by the method used by Morales et. al. [23]. A mixture of commercial-grade Fe₂O₃ and molybdenite concentrate, supplied by Uddeholms AB, were used instead of Fe₂MoO₄ for the large scale trials (and also in some laboratory scale experiments). The latter mixture is denoted as “Fe₂MoO₄ precursor” in this work. The possibilities of Fe₂MoO₄ formation from the mixture after more than 16 h heating at 1373 K was successfully confirmed by XRD analysis.

The dolomite mineral (21 % MgO, 29 % CaO, 2.3 % SiO₂, 0.44 % Al₂O₃+FeO and the rest is CO₂) was delivered by Dokshytsy mines in Belarus and limestone was provided by SSAB, Oxelösund, Sweden. Thermogravimetric studies on the decomposition of the limestone sample showed a mass loss of 43.3 %. This corresponds approximately to the loss of stoichiometric amount of CO₂ indicating that the content of CaCO₃ in the limestone is at least 98.4 %. The purity of the materials was also established by XRD analysis.

For the preparation of the master slag during slag foaming experiments, CaO (98 %), SiO₂ (99 %), MgO (99+%), and FeO (98 %) were obtained from Sigma Aldrich and Riedel-de-Haën companies, while FeO was prepared in-situ by mixing Fe₂O₃ with Fe thoroughly and pressing them into a pellet. Pure iron used for making the crucibles was obtained from ARMCO. Argon gas, purity 99.999 % was supplied by AGA gas, Stockholm. The Ar gas was purified by gas-cleaning system as follows. In order to remove the moisture, the gas was passed through silica gel columns and Mg(ClO₄)₂. CO₂ was absorbed by ascarite and traces of oxygen were removed by passing the gas through copper and magnesium turnings at 823 K and 773 K, respectively.

3.1 Thermogravimetry (TGA)

The TGA experiments were performed in SETARAM TG-24 double-furnace unit with 0.001 mg detection limit. A schematic diagram of the unit is presented in Figure 3.1.
Additionally, some of the mixtures were investigated in SETARAM-92 single furnace unit with the same accuracy.
Alumina crucibles of 8 mm inner diameter and 15 mm in height were used. The TGA analyses were carried out in Ar gas and the flow rate was varied from 46 (TG-24) to 300 (TG-92) ml/min. In the most of the experiments, the samples were heated in a non-isothermal mode at a heating rate of 10 K per minute up to the target temperatures and kept at these temperatures over a period of 10 min in order to observe the mass changes as a function of time. The observed changes were confirmed by weighing the substances before and after the experiments.
Some thermogravimetric analyses were also carried out in the isothermal mode. In these cases, a heating rate of 40 K per minute was used to reach the target temperature. The decomposition of CaMoO$_4$ was investigated at 1573, 1673, 1733, 1773 and 1823 K. In the case of MgMoO$_4$, the measurements were carried out at 1173, 1273, 1373, 1473 and 1573 K. The experimental parameters such as the amounts of the precursors and the durations of the treatment were tailored to the objectives of the individual experiments. The various
precursors, investigated in the present work, the experimental parameters, and relative mass changes are presented in Table 3.1.

Table 3.1 – Initial compositions of mixtures and relative mass changes after TGA experiments (heating rate 10 K per minute, followed by holding at 1373 K)

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Components content, wt. %</th>
<th>Mixture mass, mg</th>
<th>Holding time, min</th>
<th>Final mass decrease, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG-1</td>
<td>MoO₃ 100, CaO 73.6, MgO 28.0</td>
<td>73.6</td>
<td>10</td>
<td>95.5</td>
</tr>
<tr>
<td>TG-2</td>
<td>MoO₃ 72.0, CaO 28.0, MgO 21.7</td>
<td>479</td>
<td>10</td>
<td>1.67</td>
</tr>
<tr>
<td>TG-3</td>
<td>MoO₃ 78.3, CaO 21.7, MgO 42.2</td>
<td>484</td>
<td>10</td>
<td>0.84</td>
</tr>
<tr>
<td>TG-4</td>
<td>MoO₃ 57.8, CaO 42.2, MgO 20.0</td>
<td>445</td>
<td>10</td>
<td>17.5</td>
</tr>
<tr>
<td>TG-5</td>
<td>MoO₃ 80.0, CaO 20.0, MgO 18.4, CaCO₃ 81.6</td>
<td>70.5</td>
<td>15</td>
<td>40.9</td>
</tr>
<tr>
<td>TG-6</td>
<td>MoO₃ 61.0, CaO 23.7, MgO 15.3</td>
<td>69.4</td>
<td>15</td>
<td>24.3</td>
</tr>
<tr>
<td>TG-7</td>
<td>MoO₃ 18.4, CaO 81.6, MgO 5.0, CaCO₃ 48.9</td>
<td>63.0</td>
<td>10</td>
<td>12.2</td>
</tr>
<tr>
<td>TG-8</td>
<td>MoO₃ 46.1, CaO 5.0, MgO 48.9</td>
<td>1325</td>
<td>10</td>
<td>11.5</td>
</tr>
</tbody>
</table>

[a] - mineral calcite was used;
[b] - commercial FeOₓ and MoO₃ raw materials were supplied by Uddeholm AB, Hagfors, Sweden.

### 3.2 Gas chromatography (GC)

Evolved gas analysis experiments offered the possibility of identifying the gaseous reaction products and thereby understand the reaction mechanisms. This was carried out by gas chromatography used in the dynamic mode. The method was used to monitor the reaction between the commercial grade components in the mixture of Fe₂O₃, MoO₃ and excess carbon (mixture for Fe₂MoO₄ precursors with excess carbon) by following the off gas composition up to a maximum temperature of 1373 K. According to the mixture composition, Fe₂Mo should be the final product of reduction. A Shimadzu gas chromatograph (GC-2014 AT) with thermal conductivity detector (TCD) was employed in the present investigation. Packed stainless steel polar column with molecular sieves (3 mm i.d. and 2 m length) from Bergman Labora company, Sweden was used in the gas chromatograph. Ar was used to flush the tube at a constant flow rate (15 ml/min). The column was preconditioned for 2 hours at 423 K before the experiment. Hydrogen was used as a carrier gas for the column during the experiment. The analysis was performed with the column temperature of 423 K, injector temperature of 473 K, and sampling gas flow rate of 10 ml/min. The peaks, corresponding to Ar and CO were identified before the experiment by using the pure gases.
The reaction mixture (73.5 g) was placed above a porous alumina disc fused at the centre of a vertical quartz tube of 35 mm i.d. and 1000 mm length. The mixture was heated in a vertical furnace, equipped with Eurotherm © controller up to 1373 K with a heating rate 7 K per min. After reaching the maximum temperature of 1373 K, the mixture was kept at the constant temperature for around 200 min. During whole experiment, the Ar and CO peaks were recorded and then analyzed using the software, supplied by the GC producer. The samples were examined by XRD after the experiment.

### 3.3 High-temperature X-Ray diffraction (XRD)

In the case of the mixture of Fe$_2$MoO$_4$ precursors, it was necessary to find out the lowest temperature of formation of Fe$_2$MoO$_4$ as well as to identify the intermediate products. In order to investigate this, high-temperature X-ray diffraction studies of the Fe$_2$MoO$_4$ precursor mixture (corresponding to the sample TG-8, Table 3.1) were carried out using X'Pert PRO-PW:3040/60 X-ray diffractometer. In this experiment, a heating rate of 10 K /min was employed and Cu K$_\alpha$ radiation was used. Ar atmosphere was used for all the experiments. All the measurements were started after 10 min dwelling time at each temperature (773, 873, 973 and 1073 K) and the total exposure time was 30 min for each scan.

### 3.4 Steel alloying experiments

#### 3.4.1. Small scale experiments in laboratory

During the first step, the laboratory experiments on molybdenum yield were carried out by adding oxide mixtures to a steel bath, kept in a crucible and heated in a laboratory induction furnace in argon atmosphere. Around 16 g of steel melt was produced during each experimental heat. Both alumina and spinel crucibles were used for the laboratory experiments.

The design of the experimental arrangement is schematically presented in the Figure 3.2. The temperature of the metal was measured by an optical pyrometer, monitoring the radiation through a silica rod. The pyrometer output was fed to a PC datalogger. The temperature was controlled to an accuracy of ± 10 K by adjusting the power manually. Maximum power was used to heat the samples rapidly up to 2073 K in order to ensure complete melting of the sample. After this, the power was decreased to keep the metal at a constant temperature between 1873 and 1923 K.
Each source of Mo, studied in the present work during 16-g-scale trials, was first mixed and ground together with the stoichiometric amount of graphite powder in an agate mortar. The compositions of the alloying mixtures are listed in Table 3.2.

Table 3.2 – The compositions of alloying materials used for the 16-g-scale steel alloying trials

<table>
<thead>
<tr>
<th>Mixture N</th>
<th>Components and their content, %</th>
<th>Mass of mixture added per 16 g of iron charge, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-1</td>
<td>C-15.3; CaMoO₄-84.7</td>
<td>0.787</td>
</tr>
<tr>
<td>ST-2</td>
<td>C-16.4; MgMoO₄-83.6</td>
<td>0.733</td>
</tr>
<tr>
<td>ST-3</td>
<td>C-20.0; MoO₃-80.0</td>
<td>0.600</td>
</tr>
<tr>
<td>ST-4</td>
<td>C-15.3; MoO₃-61.0; CaO-23.7</td>
<td>0.787</td>
</tr>
<tr>
<td>ST-5</td>
<td>C-16.4; MoO₃-65.5; MgO-18.2</td>
<td>0.733</td>
</tr>
<tr>
<td>ST-6</td>
<td>C-15.0; Fe₂MoO₄-85.0</td>
<td>1.067</td>
</tr>
<tr>
<td>ST-7</td>
<td>C-15.8; MoO₂-84.2</td>
<td>0.507</td>
</tr>
<tr>
<td>ST-8</td>
<td>C-12.5; Fe₂MoO₄ precursor-87.5</td>
<td>1.279</td>
</tr>
</tbody>
</table>

Each mixture was then placed in a crucible between two tablets of pure iron, pressed from iron powder. The crucible was covered with a lid to keep the contents from spilling out in case of strong stirring during induction heating or vigorous reaction.
The duration of holding time was at least 5-6 min in order to ensure complete reaction. It was found during experiments with Fe$_2$MoO$_4$+C mixture that longer holding time (up to 20 min) did not have any impact on the yield of Mo. At the end of the experiment, the metal was gradually cooled down by power decrease. After the attainment of room temperature, all the samples were weighed and subjected to chemical analysis using X-ray fluorescence (XRF) spectroscopy.

500-g-scale laboratory experiments. Based on the results from the preliminary 16-g-scale trials, three mixtures with industrial grade components were selected for larger scale laboratory and industrial trials. The first mixture, M1, corresponds to ST-8 in Table 3.2. The mixture contains iron oxides (FeO$_x$), MoO$_3$ and C. The second one (M2, corresponds to ST-3 in Table 3.2) is the stoichiometric mixture of C and MoO$_3$, which is used as a standard, and the third one (M3, corresponds to ST-4 in Table 3.2) has an additional amount of CaO to enable CaMoO$_4$ formation.

The heats with the most prospective alloying mixtures (M1, M2 and M3) were carried out simultaneously in three crucibles with 500 g steel capacity to archive final Mo concentration 2 % and 1 % in target steel (first and second series respectively). The equipment design is schematically presented in Figure 3.3.

![Figure 3.3](image-url)
During the experiments, the alloying mixtures were charged between 2 layers (130 g and 370 g respectively) of small sized steel scrap in a crucible, casted from alumina cement. Three crucibles were heated simultaneously inside a graphite ring during each heat. A graphite cover was also used above each crucible to ensure low oxygen potential above the steel surface. The arrangement was covered by porous refractory bricks in order to provide good heat insulation. In order to monitor the temperature in the vicinity of the crucibles, a thermocouple was placed inside the graphite ring between the crucibles close to their top. By controlling the input electric power, the temperature was increased at the rate of about 10 K per minute up to 1863-1873 K. The crucibles with the contents were soaked at the experimental temperature for 20 min and then cooled down by decreasing the power. There was no inert gas protection during this experiment, as the graphite ring and covers could protect the samples. After cooling, the steel samples were extracted from crucibles, weighed and analyzed by XRF method. The compositions of the initial mixtures and their amounts are shown in Table 3.3.

<table>
<thead>
<tr>
<th>Mixture N</th>
<th>Components and their content, %</th>
<th>Mass of mixture added per 500 g of steel charge, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>first series</td>
</tr>
<tr>
<td>M1 (ST-8)</td>
<td>C-12.5; Fe₂MoO₄ precursor-87.5</td>
<td>36.0</td>
</tr>
<tr>
<td>M2 (ST-3)</td>
<td>C-20.0; MoO₃-80.0</td>
<td>16.6</td>
</tr>
<tr>
<td>M3 (ST-4)</td>
<td>C-15.3; MoO₃-61.0; CaO-23.7</td>
<td>22.2</td>
</tr>
</tbody>
</table>

### 3.4.2. Industrial trials

*Initial materials.* All raw materials and equipment for the industrial trials were provided by Uddeholms AB, Hagfors, Sweden. The mixtures and components were weighed on the balances with 1 kg detection limit. The mixing was made in a rotary mixer with 75 kg capacity. If it was not possible to put all the initial materials in the mixer for a single batch, the components of a mixture were divided in 2 portions. The amounts of initial materials, used for experimental trials, are shown in Table 3.4.

It should be noted that grinding of the initial materials was not performed during this investigation. However, for the heat H6, only small pieces of iron oxide (mostly less than 2 cm in size) were collected to make the mixture with approximately the same amount of initial materials as for the heats H1 and H2 (Table 3.4). Totally 6 portions of alloying mixtures were prepared for the experimental trials.
Table 3.4 – The amounts of initial materials used for experimental trials

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Mix No.</th>
<th>Scrap, kg</th>
<th>Mixture materials, kg</th>
<th>Slagformers, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Car scrap</td>
<td>Small sized scrap</td>
<td>FeO\textsubscript{x}</td>
</tr>
<tr>
<td>H1</td>
<td>M1</td>
<td>2004</td>
<td>1023</td>
<td>52</td>
</tr>
<tr>
<td>H2</td>
<td>M1</td>
<td>1970</td>
<td>1033</td>
<td>51</td>
</tr>
<tr>
<td>H3</td>
<td>M2</td>
<td>1992</td>
<td>990</td>
<td>0</td>
</tr>
<tr>
<td>H4</td>
<td>M2</td>
<td>1994</td>
<td>989</td>
<td>0</td>
</tr>
<tr>
<td>H5</td>
<td>M3</td>
<td>1990</td>
<td>986</td>
<td>0</td>
</tr>
<tr>
<td>H6</td>
<td>M1</td>
<td>1984</td>
<td>1022</td>
<td>51</td>
</tr>
</tbody>
</table>

[^a\] - commercial slag forming materials.

Two types of scrap were used, \textit{i.e.} pressed car scrap and small-sized scrap. Each type of scrap was weighed within 1 kg accuracy before the experiment. The compositions of both types of scrap and initial materials can be found in \textbf{Supplement 2}.

\textit{Charging sequence.} 5 ton induction furnace with 86 cm in inner diameter was used during the industrial trials. The furnace was run only for 3 ton steel capacity to provide enough safety in the case of unexpected slag foaming or vigorous reactions between the components of the mixtures. Before starting each experiment, the furnace was preheated to provide the same initial conditions for each heat. During charging, approximately 500 kg of small-sized scrap was placed first into empty hot furnace. Then, an alloying mixture was added inside steel barrels, which in turn was sealed with a lid. After that, the rest of small-sized scrap was placed above the barrel, and finally briquettes of pressed car scrap were charged above the small-sized scrap.

The sampling of metal was performed at least 2 times for each heat using standard lollypop-type sampler. The first sample was taken at 1873 K and the second one after ferrosilicon addition (10 kg) at 1943 K. The temperature of the melt was controlled with CELOX © thermocouple sensor. Slag sample was taken at least once for each heat after reaching 1873 K.

\textbf{3.5. Heat effect of slag foaming measurements}

\textit{Experimental setup.} The arrangement for heat effect studies was based on a single thermocouple-thermal analysis principle. Known amounts of the carbonate were added to slag melt and the temperature changes were recorded. The experiments had to be designed in
such a way that a quantification of the enthalpy changes could be enabled with reasonable accuracy. The experimental set up is shown in Figure 3.4.

![Figure 3.4](image)

Figure 3.4 – The experimental set-up: 1 – iron crucible with slag inside; 2 – inner thermocouple inside protective tube; 3 – outer thermocouple between crucible and furnace walls; 4 – crucible support tube; 5 – Al₂O₃ reaction tube; 6 – thermocouple for PID thermocontroller; 7 – heat isolation; 8 – conical cap from iron wires to protect top of the thermocouple projection; 9 – fallen samples

An alumina reaction tube (50 mm I.D., 60 mm O.D. and 1200 mm long) was positioned inside a vertical furnace equipped with super kanthal heating elements capable of attaining a maximum temperature of 1923 K. The furnace was controlled by a Eurotherm PID regulator to an accuracy of ± 2 K with a Rh/Pt-30 % - Rh/Pt-6 % thermocouple as the sensor. The thermocouple for furnace temperature control was placed on the outer side of the reaction tube at the level of slag surface. This arrangement was suitable as the local decrease in temperature due to carbonate addition to the slag melt had very little impact on furnace control. Preliminary experiments with two thermocouples revealed that the temperature inside the reaction tube, measured at the center point by thermocouple 3 (Figure 3.4), was not affected by more than 1-2 K during carbonate additions, which was within the accuracy of the furnace control. This could ensure that the furnace control arrangement would not have any serious impact on the present measurements of slag temperature by the core
thermocouple inside the iron crucible during carbonate additions, especially in the early stages of measurements.

Specially designed crucibles, made of ARMCO iron were used in the present study (Figure 3.4). The main feature of these crucibles is the closed-end projection inside the crucible for thermocouple, which enables more precise measurement of the temperature changes of the slag after a sample addition. The crucible was positioned inside the reaction tube so that it was in the even temperature zone of the furnace. The liquid slag surface was exposed to the cold zone of the furnace, so that a constant radiation flux was established inside the furnace. In order to protect iron crucible, purified argon gas was introduced into the furnace.

Since the radiation from a surface is proportional to the 4th power of temperature, higher experimental temperature would be preferable for the experiments. However, the maximum experimental temperature, viz. 1723 K is limited by the melting point of pure iron at 1786 K.

It was important to have a homogeneous slag phase of low viscosity in order to monitor the temperature changes fast. The master slag of the following composition was chosen after systematic study of the composition and liquidus temperature dependencies for a number of slag systems [24-25]: CaO - 31 %; SiO$_2$ - 31 %; MgO - 7 %; Al$_2$O$_3$ - 6 %; FeO - 25 %.

Samples preparation. Both spherical and wedge samples were prepared from natural materials (Figure 3.5).

Preliminary experiments showed that the experimental results were not reproducible if the carbonates, which were lighter than the slag floated on the slag surface. In order to measure the total heat effect due to the decomposition of the sample and to get reproducible results, it was found necessary that the carbonate samples sunk to the bottom of the crucible as fast as possible. In order to facilitate this, the samples were tied to sinker tablets of pure iron using thin pure iron wires. A small conical cap made of iron wire was attached to the top of the thermocouple tube inside the crucible as shown in Figure 3.4. This arrangement effectively prevented the samples landing on top of the thermocouple tube and the experiments were found to be reproducible.

Three decomposition temperatures were tested: 1623, 1673 and 1723 K. After attaining the experimental temperature, each slag was kept in the crucible for 4-5 hours before starting the experiment in order to ensure complete melting and mixing of the slag components, thereby
the homogeneity of the slag. More detailed description of the experimental setup and procedure can be found in Supplement 3.

![Figure 3.5](image)

Figure 3.5 – Samples: a – spherical limestone; b – wedge limestone; c – wedge dolomite; d – iron tablets

### 3.6. X-Ray radiography system

X-ray radiographic experiments were performed in order to observe the kinetics of foam formation. The visualization experiments were conducted on Philips BV-26 imaging system. A schematic diagram of the experimental set up is presented in Figure 3.6. The furnace assembly (Thermal Technology Inc.), with a maximum temperature of 2300 K, was equipped with graphite heating elements and alumina reaction tube. The temperature of the furnace was controlled by a Eurotherm temperature regulator within ± 2 K. The imaging system consisted of a CCD camera with digital noise reduction. A detailed description of the apparatus is presented in earlier reports from the present division [26]. Alumina crucible of i.d. 36 mm and 60 mm height was used to hold the slag. The following composition was chosen for the synthetic slag studied at 1773 K: Al₂O₃ – 20.0 %, MnO – 15.0 %, CaO – 32.5 %, SiO₂ – 32.5 %. The synthetic slag amount was 34.5 g.

21
The particles of natural limestone were introduced into the slag at 1773 K in a paper container, attached to a silica rod. The process was continuously recorded on video, after which the single screenshots were analyzed. More detailed information about the experiment can be found in Supplement 4.

3.7. Plant trials on slag foaming

The plant trials were conducted in a 100-ton EAF furnace with 75 MWh power supply (produced by Danieli ©) at Belarusian Steel Works (BMZ). Most of the heats had approximately 1 hour tap-to-tap time and 90-95 % of steel scrap in a charge. The investigation of the influence of dolomite and limestone additions on an energy balance of a heat in an EAF was performed in 2 steps. During the first stage, statistical methods of data analysis were employed. To find out the influence of limestone and dolomite on the energy demand in 100-ton EAF, the heat reports with raw plant data of more than 8000 heats, conducted at Belarusian Steel Works in 2008, were collected. After that, the filtering was performed to fetch only the heats with a certain range of other important parameters, which can have influence on energy demand (all heats without technical time-breaks, charge mass – 120 ± 3 ton, two basket scrap charge, etc.).
To clarify the influence of carbonates among more than 100 parameters on energy consumption, all the heats were normalized to the middle values of parameters. The normalization includes the elimination of the “noise” influence of the parameters with the known impact to the energy demand. More detailed information about normalization procedure can be found in Supplement 4.

As the relative time of carbonate addition in EAF can influence the energy consumptions, the parameter $t_Q$, describing the dimensionless time of carbonate addition, was introduced for each heat as:

$$
t_Q = \frac{\sum_{i=1}^{\text{vol}} Q^\text{carb}_i \cdot m^\text{carb}_i}{Q^\text{tot} \cdot m^\text{carb}_\text{tot}} \cdot 100\%,
$$

where $Q^\text{carb}_i$ – integral energy consumption by the moment of addition of $i$ portion of carbonate, J; $m^\text{carb}_i$ – mass of $i$ portion of carbonate added, kg; $Q^\text{tot}$ – total energy consumption for a heat, J; $m^\text{carb}_\text{tot}$ – total mass of carbonate, added during a heat, kg.

The parameter $t_Q$ characterizes the relative time of carbonate addition in relation to whole heat duration. Then, all the heats were divided into 2 groups: first – with early addition of carbonates ($t_Q < 33 \%$) and second – with late addition ($t_Q > 50 \%$). Finally, the correlations between energy demands and carbonates consumptions were found for both of the groups.

As later addition of carbonates was found to favor the energy efficiency of EAF, 9 trial heats were performed during second step of plant investigation to prove the advantage of later dolomite addition (limestone was not available at the plant during trials). The trial heats were conducted with the fixed consumptions of raw dolomite and lime. The heats had to be run one-by-one without any interruption or technical time breaks within the trial period. The same type of scrap (car and carbon steel scrap) was used for all of the heats during the experiment. The slag chemistry and amount were kept very nearly the same. It was found after slag analysis, that slag basicity, defined as $(\% \text{CaO})/(\% \text{SiO}_2)$ was about 2 and FeO concentration was in the range of 19-23 % for all of the heats. All heats were tapped after reaching the steel bath temperature of 1893 K.
4. Results and discussion

4.1. The development of new precursor for steel alloying with Mo

4.1.1. CaMoO$_4$, MgMoO$_4$ and Fe$_2$MoO$_4$ stabilities with respect to evaporation and oxidation

Fe$_2$MoO$_4$ stability by TGA. Pure iron molybdate (Fe$_2$MoO$_4$) was tested both in argon and air atmosphere while heating up to 1573 K with 10 K per minute rate. The results are shown in Figure 4.1. During heating in air, Fe$_2$MoO$_4$ is subjected to oxidation, which starts after 573-673 K and results in the mass increase followed by decrease. The peak of mass increase, compared to initial mass of Fe$_2$MoO$_4$, is around 12 % which can be explained by the oxidation of Fe$_2$MoO$_4$ into MoO$_3$ and Fe$_2$O$_3$ mixture according to the equation:

$$\text{Fe}_2\text{MoO}_4 + \text{O}_2 = \text{Fe}_2\text{O}_3 + \text{MoO}_3$$  \hspace{1cm} (4.1)

According to stoichiometry, the process should lead to the 11.8 % of mass increase. After reaching of 1173 K, the mass of mixture starts to decrease, probably due to the subsequent MoO$_3$ evaporation from the mixture. By the end of the experiment, the total mass changes indicate the evaporation of approximately 43 % of MoO$_3$, formed as a result of iron molybdate oxidation by air.

It should be noted that there is no mass change for Fe$_2$MoO$_4$ during the same heat treatment in the argon atmosphere, and this substance seems to be very stable source of molybdenium in the absence of oxygen (Figure 4.1).
The results of evaporation rates determination in isothermal mode as a function of reciprocal temperature are presented at Figure 4.2.

![Figure 4.2](image)

Figure 4.2 – The experimental evaporation rate \( V_{\text{evap}} \), determined in isothermal modes: 1-\( \text{MoO}_3 \); 2-\( \text{MgMoO}_4 \); 3-\( \text{CaMoO}_4 \); 4-\( \text{CaMoO}_4 \), additional series

It was found from the calculations based on available thermodynamic data from [27-28], that the sequence of evaporation rates is in agreement with the sequence in the equilibrium partial pressures of \( \text{MoO}_3 \) for each substance (see also previous chapter 2.1.2).

4.1.2. The possibilities of \( \text{CaMoO}_4 \), \( \text{MgMoO}_4 \) and \( \text{Fe}_2\text{MoO}_4 \) in-situ formation from industrial grade materials

The formations of \( \text{CaMoO}_4 \), \( \text{MgMoO}_4 \) and \( \text{Fe}_2\text{MoO}_4 \) from the mixture of initial materials were studied by TGA and high-temperature XRD facilities.

*\( TGA \) studies of \( \text{CaMoO}_4 \) and \( \text{MgMoO}_4 \) formation.* The results from the non-isothermal TGA investigations of the mixtures of \( \text{MgO} \), \( \text{CaO} \) and \( \text{CaCO}_3 \) with \( \text{MoO}_3 \) are presented in Figure 4.3. It can be seen that, in the case of mixtures of \( \text{MoO}_3 \) with \( \text{CaO} \) or \( \text{MgO} \), only a minor part of \( \text{MoO}_3 \) evaporated below 1373 K (the weight loss was about 1.8 \% in the case of \( \text{CaO} \) and even less for \( \text{MgO} \)).
Figure 4.3 – The mass changes for pure MoO$_3$ (1) and its mixtures with CaO and MgO by TGA studies: 1-MoO$_3$; 2-CaO+MoO$_3$ ($\Delta m$ multiplied by 50); 3-MgO+MoO$_3$ ($\Delta m$ multiplied by 100); T–temperature ramp in K (on right hand side Y-axis)

It can be concluded from Figure 4.3, that the formation of corresponding molybdates goes much faster than the evaporation of pure MoO$_3$. This is in conformity with the results of high temperature XRD in the case of CaO-MoO$_3$.

TGA studies of Fe$_2$MoO$_4$ formation.

TGA studies of the binary mixtures showed that in the case of MoO$_3$+C mixture two steps of mass change were observed (ca 900 and 1250 K respectively, line 3, Figure 4.4), which can be explained by intermediate MoO$_2$ formation and agrees both with mass balance calculation and other investigations [27]. The reaction is fast enough to be almost completed within 10 min of holding at 1373 K.

The mass decrease for the Fe$_2$O$_3$+C mixture starts after 900 K (line 2, Figure 4.4) and goes without noticeable intermediate steps The reaction rate is much less than that for (MoO$_3$+C) mixture and the reduction is not complete within 10 min of holding time at 1373 K.

In the case of Fe$_2$MoO$_4$ synthesis, the mass change profile has 2 steps (line 1, Figure 4.4). The final mass decrease was 11.45 % while the theoretical value should be 11.65 % corresponding to the reduction of Fe$_2$O$_3$ and MoO$_3$ in the mixture by carbon to FeO and MoO$_2$ respectively with CO formation. The reduction is reasonably fast and, as it was found from the mass change profile that the reactions were complete within 6 min after reaching the temperature of 1373 K at a heating rate of 10 K per minute.
The first step of approximately 2.8 % of mass decrease after 900 K can be mostly attributed to the reduction of Fe(III) to Fe(II) in the mixture, which should lead to 3.1 % decrease in mass if the mixture composition and reaction stoichiometry were considered. The second phase of 8.65 % mass decrease after 1200 K can be linked mostly to the formation of Mo(IV) compounds from Mo(VI), which should lead to 8.3 % decrease. It can be expected, that first, Fe$_2$O$_3$ is reduced by carbon to FeO, followed by the reduction of MoO$_3$ to MoO$_2$ and finally, Fe$_2$MoO$_4$ would be formed. MoO$_3$ melts above 1068 K and can form an eutectic with MoO$_2$ having even a lower melting temperature [4]. However, the second step of the reduction of Mo(VI) to Mo(IV) takes place at higher temperatures than for the binary C+MoO$_3$ mixture. The reaction sequence with respect to the formation of Fe$_2$MoO$_4$ from the precursor mixture can thus be described by the following equations:

$$\text{Fe}_2\text{O}_3 + C = 2\text{FeO} + \text{CO} \quad \text{(above 773-973 K)}$$  \hfill (4.2)

$$\text{MoO}_3 + C = \text{MoO}_2 + \text{CO} \quad \text{(above 1173 K)}$$  \hfill (4.3)

SEM investigation, carried out for the Fe$_2$MoO$_4$ precursors mixture after TGA study, showed non-uniform structure with irregular-shaped small crystals. EDS analysis did not show any noticeable amount of Fe$_2$MoO$_4$ crystals. In contrast, a large amount of MoO$_2$ crystals together with traces of other Mo compounds with Fe:Mo ratios 2:3 and 1:1 were found.

Thus, there was no evidence in the TGA experiments of the formation of Fe$_2$MoO$_4$ from the mixture according to the reaction (4.4) within the short time of soaking at 1373 K:
$\text{MoO}_2 + 2\text{FeO} = \text{Fe}_2\text{MoO}_4$ \hspace{1cm} (4.4)

The comparison of these results with the synthesis of $\text{Fe}_2\text{MoO}_4$, where the samples were heated for 16 h at 1373 K, indicates that longer soaking times and higher temperatures may be required for the formation of $\text{Fe}_2\text{MoO}_4$.

*High temperature XRD studies on $\text{CaMoO}_4$ formation from CaO and MoO$_3$ mixture.* While there are no noticeable differences in the XRD diffraction peaks of the samples measured at 298 and 773 K, the peak of CaMoO$_4$ for plane of (112) index was quite prominent at 873 K. After reaching 973 K, all the reflections were in agreement with the database values corresponding to indices for the various planes of CaMoO$_4$ (Figure 4.5), thus confirming that the final product was pure CaMoO$_4$.

![Figure 4.5 – XRD patterns for the mixture of CaO with MoO$_3$ mixture at 973 K (1) and the diffraction indices for different planes of CaMoO$_4$ from XRD database (2)](image)

These observations confirmed that the formation of CaMoO$_4$ starts even at 873 K and is completed by 973 K. In a view of the less-encouraging results, the XRD studies were not carried in the case of MgMoO$_4$.

*High temperature XRD studies on $\text{Fe}_2\text{MoO}_4$ formation from precursor mixture.* There are no serious differences between XRD peaks at room temperature and 773 K. However, some small changes in XRD peaks are observed at 873 K as compared to room temperature, probably due to the chemical reactions getting started. The major phase, found after reaching
973 K was MoO$_2$. The peaks of the samples were almost the same at 973 and 1073 K, and MoO$_2$ seems to be the major component of the Fe$_2$MoO$_4$ precursors mixture treatment, together with the small amounts of iron oxides FeO, Fe$_3$O$_4$ and Fe$_2$Mo$_3$O$_8$ (Figure 4.6).

![Figure 4.6 – XRD patterns for the mixture for Fe$_2$MoO$_4$ precursor at 1073 K: 1-patterns; 2-MoO$_2$ markers; 3-Fe$_2$Mo$_3$O$_8$ markers; 4-FeO markers; 5-Fe$_3$O$_4$ markers](image)

This means that the reduction of MoO$_3$ started around 873 K and the formation of MoO$_2$ is finished before reaching 973 K. On the other hand, there was no fast reaction between MoO$_2$ and FeO at 1073 K as there were no XRD peaks corresponding to Fe$_2$MoO$_4$ found at such temperatures after 10 min holding. These results are in conformity with the TGA results. Thus, it can be concluded that the reaction of MoO$_3$ reduction by carbon includes at least 2 steps. First one is a fast reaction resulting in the formation of MoO$_2$ before 973 K, while the second stage of MoO$_2$ reaction with FeO proceeds much slower and requires more than 10 min holding time at 1273-1473 K.

### 4.1.3. The investigation of CaMoO$_4$ and Fe$_2$MoO$_4$ precursors reduction processes

**Non-isothermal TGA studies.** The results of TGA investigations on C+MoO$_3$+FeO$_x$, C+MoO$_3$ and C+MoO$_3$+CaO mixtures in argon atmosphere with the heating rate 10 K/min are shown in **Figure 4.7**. All the mixtures were constructed to provide full reduction of MoO$_3$ to metallic Mo. For both mixtures, the reduction proceeds in 2 steps with the same starting temperatures for the first step (900 K).
Figure 4.7 – The degree of carbon oxidation in carbon containing mixtures: 1 – C+FeO₃+MoO₃; 2 – C+MoO₃ mixture; 3 – C+MoO₃+CaO mixture; 4 – temperature ramp in K (on right hand side Y-axis)

In the case of binary C+MoO₃ mixture, the first step, as inferred from the mass loss, which is around 27 % of carbon mass, (theoretical mass loss should be 33.3 % of total carbon) can be attributed to the process of MoO₃ reduction to MoO₂ in accordance with the equation

\[ \text{MoO}_3 + C = \text{MoO}_2 + \text{CO} \]  \hspace{1cm} (4.5)

The results are in agreement with the earlier investigations, which confirmed that the reduction of MoO₃ to Mo by carbon proceeds step by step via MoO₂ formation [27]. The second step starts immediately after the first one, but reaches a high rate only above 1200 K. Total carbon consumption for this mixture is 88 %, and this can be related to the full reduction of MoO₃ and metallic Mo formation according to the following equation:

\[ \text{MoO}_3 + 3C = \text{Mo} + 3\text{CO} \]  \hspace{1cm} (4.6)

(maximum carbon consumption in the case of full reduction should be 100 %). The reaction is almost complete within 10 min of holding at 1373 K, as there are no mass changes afterwards.

With respect to the mechanism of reduction, C+MoO₃ mixture initially forms the intermediate oxide Mo₄O₁₁. This could dissolve in MoO₃ forming a eutectic with MoO₃, which is likely to melt at 823 K [29]. Further reduction through the liquid phase is likely to be easier.
In the case of C+MoO$_3$+CaO mixture, the reduction sequence appears to be different. The mass change for the first stage is only half in compared to the corresponding step in the case of C+MoO$_3$ mixture. This would imply that MoO$_3$ is only partially reduced. Further, the rate of reduction of intermediates by carbon during the second stage is less compared to the carbon mixture with pure MoO$_3$. This is attributed to the formation of species like CaMoO$_3$ and CaMoO$_4$ which are likely to retard further reduction to molybdenum metal.

For C+FeO$_x$+MoO$_3$ mixture, at least 2 steps can be observed on mass change curve. The first one is around 6% of total carbon demand and can be attributed to the reduction of Fe(III) in the mixture. It is clear from the Figure 4.7, that further reduction by carbon is much slower in comparison with C+MoO$_3$ mixture, probably because of formation of stable intermediate compounds.

Since the evaporation of pure MoO$_3$ is significant only above 1070 K (Figure 4.3), the reduction by carbon (after 900 K) or reaction with CaO (after 873 K) will precede the evaporation step thus stabilizing Mo in the condensed phase.

Gas chromatograph (GC) studies. Gas chromatograph studies were carried out only for Fe$_2$MoO$_4$ precursor mixture. The results of composition changes of gas, passed through the heated mixture are shown in Figure 4.8 as a function of furnace temperature.

![Figure 4.8](image-url) – The gas composition changes as a function of mixture temperature: 1 – CO peak intensity; 2 – Ar peak intensity; 3 – temperature profile
It can be seen in the Figure 4.8 that argon concentration starts to decrease just above 800 K, probably due to the dilution of gas mixture with CO$_2$ formed by carbon oxidation (this could not be detected by GC) during the experiment. After 1110 K, a sharp increase in CO concentration is observed. The evolution of CO reaches its maximum at approximately 1300 K and then starts to decrease. The decrease lasts for the whole experiment, probably due to the large volume of the reactor tube and small gas flow rate.

The XRD patterns of the product of Fe$_2$MoO$_4$ reduction after GC experiment are shown in Figure 4.9.

![Figure 4.9 – The XRD patterns of the products after gas chromatograph experiment: 1-Mo$_{18}$C$_7$; 2-Mo$_2$C; 3-C; 4-Fe$_7$Mo$_3$; 5-Mo](image)

It is clear from Figure 4.9 that the XRD peaks for the solid products of GC experiment indicate the presence of metallic Mo, intermetallic Fe$_7$Mo$_3$ and carbides Mo$_2$C and Mo$_{18}$C$_7$. The partial formation of carbides during long heating can be explained by a certain amount of excess carbon in the mixture.

4.1.4. Laboratory trials on steel alloying from 16-g- to 500-g-scale experiments

16-g-scale laboratory experiments. During the 16-g-scale experiments, most of the samples showed the concentration of Mo around 2% after the trials. There was no noticeable crucible contamination as well as metal loses in any form. To compare the results from different heats, molybdenum yield was estimated from each sample analysis. Analysis from different parts of the sample showed similar Mo contents, confirming thereby that the Mo distribution in the sample was uniform. The molybdenum yield could be calculated as the ratio of molybdenum mass in the metal sample to the mass of molybdenum in the initial mixture:
\[ \eta_{\text{Mo}} = \frac{[\% \text{Mo}]_{\text{met}} \cdot m_{\text{met}}}{[\% \text{Mo}]_{\text{mix}} \cdot m_{\text{mix}}} \cdot 100\% , \]  

(4.7)

where \([\% \text{Mo}]_{\text{met}}\) – molybdenum content in a metal sample, \(m_{\text{met}}\) – metal sample mass, \([\% \text{Mo}]_{\text{mix}}\) – molybdenum content in alloying mixture, \(m_{\text{mix}}\) – alloying mixture mass.

The experiments showed that, after 4-5 min after reaching 1923 K, the steel samples were homogeneous, the mixture was completely consumed and the yield of Mo reached the values up to 98%. This indicated that the dissolution of molybdenum in liquid iron is fast enough and nearly completed during the melting of the iron tablets. It should also be mentioned that the mass changes observed before and after the experiments by weighing the crucibles were in good agreement with the mass balance of the full reduction of molybdenum source by carbon with metallic Mo formation for both completely and partially melted samples. The comparison of average values of molybdenum yield for different molybdenum precursor, tested in present work, is shown in the Table 4.1.

**Table 4.1** – The average values of molybdenum yield, obtained from the different molybdenum sources in 16-g-scale test

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Molybdenum precursor</th>
<th>Number of reliable experiments</th>
<th>Average value of the yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-1</td>
<td>CaMoO₄+C</td>
<td>3</td>
<td>93.0</td>
</tr>
<tr>
<td>ST-3</td>
<td>MoO₃+C</td>
<td>4</td>
<td>93.3</td>
</tr>
<tr>
<td>ST-4</td>
<td>CaO+MoO₃+C</td>
<td>3</td>
<td>92.0</td>
</tr>
<tr>
<td>ST-5</td>
<td>MgO+MoO₃+C</td>
<td>4</td>
<td>6.6</td>
</tr>
<tr>
<td>ST-6</td>
<td>Fe₂MoO₄+C</td>
<td>2</td>
<td>98.2</td>
</tr>
<tr>
<td>ST-7</td>
<td>MoO₂+C</td>
<td>3[⁠a]</td>
<td>93.2</td>
</tr>
<tr>
<td>ST-8</td>
<td>Fe₂MoO₄ precursor+C</td>
<td>1</td>
<td>95.4</td>
</tr>
<tr>
<td>ST-8</td>
<td>Fe₂MoO₄ precursor +C</td>
<td>3[⁠a]</td>
<td>96.2</td>
</tr>
</tbody>
</table>

[⁠a⁠]-experiments with spinel crucibles

The results showed that both prepared Fe₂MoO₄ and Fe₂MoO₄ precursor mixture provided the highest yield during laboratory steel trials, which can be explained by the absence of molybdenum evaporation from this alloying material in argon atmosphere. These results are in agreement with thermogravimetric studies, described in previous chapter. It should also be noted that both Fe₂MoO₄ and Fe₂MoO₄ precursor mixtures easily react with iron during melting. The product particles were found to be strongly adhering to the iron surface in the case of partially melted samples, which indicated the affinity between iron surface and the precursor. On the contrary, in the case of CaMoO₄, as well as precursors mixtures
CaO+MoO₃ and MgO + MoO₃, the products didn’t have any adhesion to the metal surface and could easily be separated from the metal after the experiment.

500-g-scale laboratory experiments. The 500-g-scale experiments were carried out as the second stage of the process development. Post-experiment observations revealed that the metal had completely melted without any appreciable evidences of crucibles contaminations. The results of the Mo yield calculations after the samples analysis are shown in Table 4.2.

Table 4.2 – The values of molybdenum yield, obtained during 500-g-scale experiment

<table>
<thead>
<tr>
<th>Mixture N</th>
<th>Components and their content, %</th>
<th>Mo yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1ˢᵗ series</td>
</tr>
<tr>
<td>M1</td>
<td>C-12.5; Fe₂MoO₄–precursor-87.5</td>
<td>97.7</td>
</tr>
<tr>
<td>M2</td>
<td>C-20.0; MoO₃-80.0</td>
<td>93.0</td>
</tr>
<tr>
<td>M3</td>
<td>C-15.3; MoO₃-61.0; CaO-23.7</td>
<td>76.6</td>
</tr>
</tbody>
</table>

ᵃ -There was a leakage of steel from this crucible and the Mo yield obtained is not reliable.

The results showed that M1 (Fe₂MoO₄ precursor+C) mixture provides the highest yield, which is in agreement with the smaller scale experiments. The yield from MoO₃+C mixture is approximately the same as for 16-g-scale trials, while for CaO+MoO₃+C mixture the yield is considerably lower. The poor yield and scattering of the results during 500-g-scale trials for the M3 mixture may be attributed to incomplete reaction between the components of the mixture and steel.

4.1.5. Industrial trials on steel alloying in 3 ton induction furnace

In the case of plant trials at 3 ton scale, it could be concluded by monitoring the power consumption that the melting of the scrap started after 30-40 min after small-sized scrap charging. The heating rate was estimated from this to be 35-50 K per min, which is 3-5 times higher than for the 500-g-scale laboratory trials. At the same time, considerable flame was observed, most probably due to CO evolution from the furnace. This was not observed during usual heats with similar type of scrap but without such alloying mixtures addition.

It should be noted that most of the samples, which were taken after complete scrap melting but before silicon addition, had poor quality (hollow metal), which resulted in limited possibilities for chemical analysis. Mainly, the samples after ferrosilicon addition were considered during the investigation. After the chemical analysis of the samples, the yield of Mo was calculated for each heat using the formula (4.7). Additionally, the mass of liquid
slag was calculated based on known amount of CaO input and CaO concentration in final slag:

\[ m_{\text{slag}} = \frac{\sum m_i \cdot w_{i}}{w_{\text{CaO}^{\text{slag}}}}, \]

where \( m_{\text{slag}} \) – slag mass, \( m_i \) – mass of added material \( i \), \( w_i \) – CaO content in the added material \( i \), \( w_{\text{CaO}^{\text{slag}}} \) – CaO content in slag after addition. The results of steel samples analysis and molybdenum yield together with other parameters calculations are presented in Table 4.3. The slag compositions of the experimental heats are presented in Table 4.4. It is seen from the Table 4.3 that the concentrations of Mo in slag were very low for all of the heats.

Table 4.3 – The results of steel samples analysis and molybdenum yield calculations

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Mix No.</th>
<th>Metal composition, %</th>
<th>Calculated parameters</th>
<th>Liquid steel, kg</th>
<th>Slag mass, kg</th>
<th>Mo yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mo</td>
<td>C</td>
<td>Mn</td>
<td>Si</td>
<td></td>
</tr>
<tr>
<td>H1</td>
<td>M1</td>
<td>0.9</td>
<td>0.065</td>
<td>0.17</td>
<td>0.13</td>
<td>2936</td>
</tr>
<tr>
<td>H2</td>
<td>M1</td>
<td>0.91</td>
<td>0.077</td>
<td>0.39</td>
<td>0.29</td>
<td>2917</td>
</tr>
<tr>
<td>H3</td>
<td>M2</td>
<td>0.94</td>
<td>0.083</td>
<td>0.2</td>
<td>0.15</td>
<td>2894</td>
</tr>
<tr>
<td>H4</td>
<td>M2</td>
<td>0.93</td>
<td>0.05</td>
<td>0.14</td>
<td>0.015</td>
<td>2891</td>
</tr>
<tr>
<td>H5</td>
<td>M3</td>
<td>0.93</td>
<td>0.046</td>
<td>0.14</td>
<td>0.002</td>
<td>2884</td>
</tr>
<tr>
<td>H6</td>
<td>M1</td>
<td>0.992</td>
<td>0.079</td>
<td>0.21</td>
<td>0.26</td>
<td>2922</td>
</tr>
</tbody>
</table>

Table 4.4 – The results of slag analysis for the experimental trials

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Mix No.</th>
<th>Slag composition, %</th>
<th></th>
<th>CaO</th>
<th>FeO</th>
<th>MnO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>MgO</th>
<th>Cr₂O₃</th>
<th>MoO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>M1</td>
<td>23.6</td>
<td>21.3</td>
<td>15.1</td>
<td>19.1</td>
<td>10.0</td>
<td>4.07</td>
<td>2.97</td>
<td>0.0623</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>M1</td>
<td>28.8</td>
<td>11.0</td>
<td>12.0</td>
<td>15.9</td>
<td>15.9</td>
<td>7.77</td>
<td>2.32</td>
<td>0.0740</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H3</td>
<td>M2</td>
<td>27.8</td>
<td>14.7</td>
<td>13.1</td>
<td>18.0</td>
<td>13.5</td>
<td>5.77</td>
<td>3.12</td>
<td>0.0628</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H4</td>
<td>M2</td>
<td>23.1</td>
<td>22.8</td>
<td>13.8</td>
<td>20.8</td>
<td>7.24</td>
<td>3.97</td>
<td>1.47</td>
<td>0.0817</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H5</td>
<td>M3</td>
<td>24.2</td>
<td>22.6</td>
<td>13.0</td>
<td>19.5</td>
<td>7.49</td>
<td>7.18</td>
<td>2.05</td>
<td>0.0675</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H6</td>
<td>M1</td>
<td>24.8</td>
<td>18.2</td>
<td>14.4</td>
<td>18.2</td>
<td>11.5</td>
<td>5.05</td>
<td>1.87</td>
<td>0.0570</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

MoO₃+C+FeOₓ mixture (M1). In the case of this MoO₃+C+FeOₓ mixture, 3 heats were performed with the same charging mixture and the Mo yields were quite scattered depending on the mixture preparation. For the heats H1(M1) and H2(M1) Mo yield was 89.2 % and 91.5 % respectively. For these heats, large initial pieces of iron oxide were used. Some of the pieces were more that 10 cm in size. Further, poor mixing because of mixer overloading
and partial loss of materials when mixing them without lid could be the reason for the lowest yield in the case of the first heat H1(M1).

Since it was presumed that larger pieces of iron oxide would result in incomplete formation of iron molybdate in the mixture due to the low surface area to volume ratio, for the heat H6(M1) mainly small pieces (below 2 cm in diameter) were taken during mixture preparation. The yield of Mo for H6(M1) heat reached 97.8 %.

\textit{MoO}_3+C \textit{mixture (M2)}. According to the plant results, the Mo yield for the heat H3(M2) is 92.8 % and for H4(M2), it is 92.6 % and the results are reproducible. The same values (around 93 %) of Mo yield were obtained during the laboratory tests with 16 g and 500 g crucible capacities (Tables 4.1 and 4.2).

\textit{MoO}_3+C+CaO \textit{mixture (M3)}. The Mo yield of the heat H5(M3) is 92.4% and the mixture was tested in only one heat. This yield is closed to the lab results with 16 g heat size (Table 4.1). The lowest Mo yield for the lab results were observed in the case of 500 g crucible capacity (Table 4.2) experiments. This could be due to the experimental design adopted and consequent insufficient dissolution of the molybdate formed without getting dissolved in the metal bath. The high yield of Mo during heat H5 shows that such mixtures might also be promising as Mo precursors in EAF. Further trials to investigate this are currently under progress.

4.2. Slag foaming caused by carbonates decomposition

4.2.1. Thermodynamic modeling results

In order to estimate the energy saving effect, the amount of heat, required for the process of both decomposition and heating of the products from 298 to 1673 K need to be estimated. The heat capacities were taken into account by using the equation (4.9):

\[ \int_{T_1}^{T_2} C_P dT = a(T_2 - T_1) + \frac{1}{2} b \cdot 10^{-3} \cdot (T_2^2 - T_1^2) + \frac{1}{3} c \cdot 10^{-6} \cdot (T_2^3 - T_1^3) - d \cdot 10^5 (\frac{1}{T_2} - \frac{1}{T_1}), \quad (4.9) \]

where a, b, c and d are the terms in heat capacity equation, J/K^2·mol, J/K^3·mol, J/mol and J/K^4·mol respectively. The calculations were also checked using Thermocalc software (Version S, SGTE Solutions database v.4). The calculated values of decomposition energies are presented in Table 4.5.
Table 4.5 – The results of the calculations of the heat demand for the carbonates decomposition and products heating from 298 to 1673 K

<table>
<thead>
<tr>
<th>Source of calculations</th>
<th>Dolomite energy demand, J/g</th>
<th>Limestone energy demand, J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔH_r^{298}</td>
<td>Products heating</td>
</tr>
<tr>
<td>Thermocalc software</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Version S, SGTE Solutions database v.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculations based on literature data [30]</td>
<td>1545.4</td>
<td>1568.3[^c]</td>
</tr>
</tbody>
</table>

[^a] - heating CaCO_3 from 298 to 1127 K  
[^b] - heating CaO and CO_2 from 1127 to 1673 K  
[^c] - heating CaO, MgO and CO_2 from 298 to 1673 K

For further discussions, the calculations carried out by the author based on the C_p values reported in [30] are used.

4.2.2. Measured energies of decomposition for natural limestone and dolomite

*Calibration curves.* In the case of well-stirred liquid bath, the temperature decrease, followed by cold body immersing, should be the same at any point in the liquid and be dependent only upon the amount of heat transferred. Thus, the rate of temperature changes should be related only to the heat flux from the slag to the body surface [31]. However, the experimental profiles of slag temperature change after the addition of the calibration pieces of iron of the same mass showed different values of temperature drop as well as different initial slope of the curves (Figure 4.10). The result may have to be explained by the relatively high values of slag viscosity, which would increase further due to the temperature decrease after the samples addition. Due to the increase of viscosity and small crucible size, the convective heat transport may not play a major role in heat distribution inside the slag. In this case, the rate of temperature decrease in any particular position inside slag should depend on the relative position of thermocouple to the sample and furnace wall. As the distance between thermocouple and furnace wall is fixed, again, the rate of temperature changes should be only a function of distance between the falling sample and thermocouple. And in the case of the same positions it should be possible to compare the heat effects by the areas above temperature curves.
In the present results, it was also found that the temperature profiles are in agreement with the model of a sphere heating from the initial temperature $T_c$ to the outer temperature $T_0$. The analytical solution of this task is considered in [31]. These authors proposed the following equation for this problem:

$$T = T_0 + \frac{2RT_0}{\pi \kappa} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n \pi r}{R} e^{-\frac{4n^2 \pi^2 \kappa}{R^2} t},$$  \hspace{1cm} (4.10)

where $T$ - current temperature, $T_0$ - surface temperature, $R$ - sphere radius, $r$ - distance from the center, $t$ – time, $s$; $\kappa$ - thermodiffusivity coefficient, m$^2$/s.

$$\kappa = \frac{K}{\rho C_p},$$  \hspace{1cm} (4.11)

where $K$ – thermal conductivity, W/(m·K); $\rho$ - slag density, kg/m$^3$; $C_p$ – slag heat capacity, J/(kg·K).

By using the equation (4.10), one can obtain the description of temperature profile for any distance from the center of the sphere. From preliminary estimations [31], the experimental slag heat conductivity was found to be 0.15 W/(m·K). Using the following boundary conditions (at $t=0$ and $r=0$ $T_c=T_0-\Delta T_{\text{max}}$; at any $t$ and $r=R$ $T=T_0$) together with data on slag heat conductivity, density and heat capacity, it is possible to estimate the change of temperature inside a sphere with time. The results of the comparison between calculated and experimental temperature changes for the calibration experiments with iron tablets are also shown in Figure 4.10. As a first approximation $\Delta T_{\text{max}}$ was assumed to be equal to the maximum temperature drop, observed during experiments.

It is clear from Figure 4.10, that, with the lapse of a short time after the dropping of the iron tablet ($t>0.04 \cdot \frac{r^2}{\kappa}$), the change in temperature is in agreement with the model curve. This would validate that the process of heat transfer can be described by the model of sphere heating, if time $t > 0.04 \cdot \frac{r^2}{\kappa}$.

Thermal analysis. Each experimental curve for sample addition was matched with a corresponding calibration one of same initial slope in the same series. The examples are shown in Figure 4.11.
The heat effects of dolomite and limestone decomposition were calculated in relation to “iron equivalent” by comparison of the areas above calibration and experimental curves according to the equation:

\[ Q_{\text{foam}} = Q_{Fe} \cdot \frac{S_2 - S_1}{S_1}, \]  

(4.12)

where \( Q_{\text{foam}} \) – heat effect of slag foaming (which corresponds to the endothermic heat due to the decomposition plus the heat insulation effect due to foam formation), \( Q_{Fe} \) – heat required for heating of calibration piece of iron to experimental temperature, \( S_1 \) – the area above the most suitable calibration curve, \( S_2 \) – the area above the experimental curve. The amount of heat, required for iron to be heated, was calculated on the basis of equations (4.9) and (4.13) [30]:

\[ H_{T_f} - H_{T_i} = \sum_{T_i}^{T_f} C_p dT + \sum \Delta H_{tr}, \]  

(4.13)

where \( H_T \) – substance enthalpy at the temperature \( T \), J/mol; \( C_p \) – the heat capacity of the substance, J/K·mol; \( \Delta H_{tr} \) – the enthalpy change for a phase transition, J/mol.
The total heat effect of slag foaming due to carbonates decomposition was evaluated on the basis of the following assumptions:

- the dissolution of CaO and MgO results in 1 mm decrease in diameter for 15 min staying in slag at 1673 K. Only CaO dissolution has appreciable effect on the system enthalpy change and the enthalpy change for solid CaO dissolution is - 936 J/g for CaO for the experimental slag composition at 1673 K as it was found in HS Chemistry software. According to some investigations, for the similar slag basicity and FeO content [32], the rate of dissolution of MgO from burned dolomite is few times slower comparing to CaO;
- additions of carbonates do not affect slag properties significantly. Viscosity calculations, performed with the aid of the models in literature [33], showed that the additions of 3 g of dolomite and 3 g of limestone should result in decrease of the slag viscosity of approximately 4.3 % at 1723 K, 4.5 % at 1673 K and 4.7 % at 1623 K. There are no noticeable changes in slag density at the same time as estimated by the density model developed in the present laboratory [34];
- the area above the thermal analysis curve is largely proportional to the amount of heat, required both for heating and decomposition of the sample if the relative position of the sample and thermocouple is the same for all of experiments;
- the only mass change during slag foaming was due to the escape of CO\textsubscript{2} gas. The mass balance for each crucible was checked before and after an experiment. For the temperatures 1623-1673 K, the mass difference was no more than 5% from the expected mass change. However, at 1723 K, the agreement became very poor and the results of heat effect measurements showed big scatter. And a significant amount of oxide powder was found scattered outside crucibles after the experiment probably caused by the splashing of the slag. This can only be explained by a vigorous reaction of decomposition at this temperature. Hence, the results for 1723 K were not considered, and for 1673 K, the results with the values of decomposition energy, which were found to be 20% lower than the average value, were excluded from the consideration to avoid any possible errors. More detailed information about curve matching technique, assumptions and initial data can be found in the Supplement 3. The measured and calculated total heats for the carbonates decomposition, together with possible dissolution effect for CaO, are presented in Table 4.6.

Table 4.6 – Calculated and measured heat effects of dolomite and limestone decomposition

<table>
<thead>
<tr>
<th>Substance</th>
<th>T, K</th>
<th>Calculated carbonate decomposition energy, kJ/kg</th>
<th>Measured heat of carbonates decomposition, kJ/kg</th>
<th>Measured heat of carbonates decomposition, % from calculated values</th>
<th>Measured heat of carbonates decomposition together with CaO dissolution effect\textsuperscript{[a]}, % from calculated values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
<td>From</td>
<td>To</td>
<td>From</td>
</tr>
<tr>
<td>Dolomite</td>
<td>1623</td>
<td>3146.6</td>
<td>1731.9</td>
<td>2187.6</td>
<td>53.0</td>
</tr>
<tr>
<td></td>
<td>1673</td>
<td>3213.7</td>
<td>1801.6</td>
<td>2370.5</td>
<td>54.9</td>
</tr>
<tr>
<td></td>
<td>1723</td>
<td>3281.5</td>
<td>492.7</td>
<td>689.8</td>
<td>15.0</td>
</tr>
<tr>
<td>Limestone</td>
<td>1623</td>
<td>3251.7</td>
<td>2005.3</td>
<td>2278.8</td>
<td>58.9</td>
</tr>
<tr>
<td></td>
<td>1673</td>
<td>3318.9</td>
<td>1896.4</td>
<td>2180.9</td>
<td>55.6</td>
</tr>
<tr>
<td></td>
<td>1723</td>
<td>3386.9</td>
<td>492.7</td>
<td>689.8</td>
<td>14.5</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]}- the effect for CaO dissolution was calculated assuming 1 mm decrease in diameter (for spherical shape) or in sizes (for wedge shape) of the samples within 15 min of the experiment duration. The enthalpy of CaO dissolution was calculated to be 936 kJ/kg.

The results showed that the experimental values of decomposition energies are in the range of 55-74% from the theoretical ones. The enthalpy of CaO dissolution would affect the
values by 59-79 % for dolomite and 62-70 % for limestone from theoretical energy demand at 1673 K. It should be noted that at 1623 K, no decrease in samples size was observed, thus, the CaO dissolution effect should be much smaller. Further, the energy of decomposition seems to be approximately the same both for dolomite and limestone, which differ by about 2 times in CaO content. The differences between measured and calculated values of carbonates decomposition energies are attributed mostly to the energy saving effect of slag foaming on total energy balance.

4.2.3. Plant data analysis
As it was found from the analysis of the data on the first step of the plant investigation, both raw dolomite and limestone lead to increase in energy demand in an EAF. However, the effect is different depending on relative time for carbonate addition. If carbonate is added during early stage of heat (when $t_Q < 33 \%$), when the specific energy consumption is around 2 times higher compare to the addition of carbonates into EAF at the later stage (Figure 4.12). In the case of later addition (when $t_Q > 50 \%$), the heat effects for limestone and dolomite (2255 and 2264 kJ/kg respectively, Figures 4.12c and 4.12d) are quite close to the values, determined during laboratory experiments (Supplement 4). That means the saving of at least 30 % of energy, required for carbonate decomposition, when carbonates are added at the later stage of a heat (liquid steel bath) in an EAF.

On the second step of the plant trials, the studies were focused on the dolomite influence on the energy consumption. Two series of trial heats (totally 9 heats with the controlled amounts of lime and dolomite) were conducted. The parameters and results of the trial (1st-2nd series) and reference (3rd series) heats are presented in Table 4.7 and the mean values of the results – in Table 4.8.

It was found from the trial heats with later dolomite addition that the partial substitution of lime with raw dolomite does not lead to the increase in energy consumption. At the same time, it is also important to keep a certain amount of slag on the metal surface, otherwise the energy demand can even increase even if the specific consumption of lime will be low (series N 2).

One additional benefit from the dolomite usage in an EAF is the CO$_2$ involvement as an oxidant gas in the process. If dolomite is decomposed inside the slag, it can act as an additional oxidant gas for carbon in steel:

$$[C] + [CO_2] = 2[CO] \quad (4.14)$$
Further, *in-situ* CaO formation and additional mixing because of gas evolution can promote other reactions. For example, plant trial results showed a small but definite further-lowering of phosphorus concentration to about 0.0033 % in steel in the case of partial lime substitution with dolomite.

**Table 4.7 – The parameters of the trial and reference heats**

<table>
<thead>
<tr>
<th>Series N</th>
<th>Heat N</th>
<th>Slagformers supply, kg</th>
<th>Normalized energy demand, J/ton (×10⁹)</th>
<th>Arc operation time, min</th>
<th>Liquid steel weight, ton</th>
<th>Oxygen supply, m³/ton</th>
<th>Fuel gas supply, m³/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>3559</td>
<td>1.375</td>
<td>41</td>
<td>114</td>
<td>3119</td>
<td>977</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3500</td>
<td>1.354</td>
<td>40</td>
<td>113</td>
<td>3217</td>
<td>970</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3621</td>
<td>1.316</td>
<td>42</td>
<td>116</td>
<td>2903</td>
<td>945</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>3634</td>
<td>1.533</td>
<td>44</td>
<td>106</td>
<td>2950</td>
<td>919</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>3041</td>
<td>1.457</td>
<td>45</td>
<td>110</td>
<td>2846</td>
<td>1078</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>3030</td>
<td>1.461</td>
<td>47</td>
<td>114</td>
<td>3065</td>
<td>1148</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>3064</td>
<td>1.266</td>
<td>48</td>
<td>108</td>
<td>3176</td>
<td>1097</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>3030</td>
<td>1.310</td>
<td>44</td>
<td>120</td>
<td>3148</td>
<td>1180</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>3039</td>
<td>1.574</td>
<td>46</td>
<td>109</td>
<td>3164</td>
<td>1172</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>3561</td>
<td>1.172</td>
<td>44</td>
<td>111</td>
<td>3143</td>
<td>932</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>3802</td>
<td>1.344</td>
<td>43</td>
<td>109</td>
<td>2994</td>
<td>1089</td>
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<tr>
<td>12</td>
<td>12</td>
<td>3704</td>
<td>1.218</td>
<td>43</td>
<td>114</td>
<td>2881</td>
<td>1069</td>
</tr>
<tr>
<td>13</td>
<td>13</td>
<td>3904</td>
<td>1.065</td>
<td>44</td>
<td>120</td>
<td>3058</td>
<td>1090</td>
</tr>
<tr>
<td>14</td>
<td>14</td>
<td>3932</td>
<td>1.461</td>
<td>43</td>
<td>109</td>
<td>3398</td>
<td>1283</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>3915</td>
<td>1.663</td>
<td>47</td>
<td>103</td>
<td>3155</td>
<td>1153</td>
</tr>
<tr>
<td>16</td>
<td>16</td>
<td>3936</td>
<td>1.671</td>
<td>47</td>
<td>112</td>
<td>3433</td>
<td>1190</td>
</tr>
<tr>
<td>17</td>
<td>17</td>
<td>3839</td>
<td>1.517</td>
<td>46</td>
<td>108</td>
<td>3258</td>
<td>1182</td>
</tr>
<tr>
<td>18</td>
<td>18</td>
<td>3834</td>
<td>1.560</td>
<td>45</td>
<td>105</td>
<td>3035</td>
<td>1083</td>
</tr>
<tr>
<td>19</td>
<td>19</td>
<td>3467</td>
<td>1.288</td>
<td>44</td>
<td>118</td>
<td>3124</td>
<td>1108</td>
</tr>
</tbody>
</table>

**Table 4.8 – The mean values of the trial and reference heats**

<table>
<thead>
<tr>
<th>Series N</th>
<th>Lime, kg/ton</th>
<th>Dolomite, kg/ton</th>
<th>Total slagformers, kg/t</th>
<th>Heat duration, min</th>
<th>Fuel gas, m³/ton</th>
<th>Oxygen, m³/ton</th>
<th>Normalized energy, J/ton (×10⁹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31.9</td>
<td>9.4</td>
<td>36.6[b]</td>
<td>41.6</td>
<td>952.8</td>
<td>3047.3</td>
<td>1.394</td>
</tr>
<tr>
<td>2</td>
<td>27.1</td>
<td>7.9</td>
<td>31.1</td>
<td>46</td>
<td>1135</td>
<td>3079.8</td>
<td>1.413</td>
</tr>
<tr>
<td>3</td>
<td>34.3</td>
<td>2.2[a]</td>
<td>36.5</td>
<td>44.6</td>
<td>1118.1</td>
<td>3147.9</td>
<td>1.396</td>
</tr>
</tbody>
</table>

[a] - for the reference heats only burned dolomite was used in addition to lime;

[b] - the value was calculated by taking into account the raw dolomite mass change after decomposition.
4.2.4. Studies on the kinetics of slag foaming and modeling of the foam height changes

Typical X-ray images obtained in the present study with the addition of 1-3 mm fractions of limestone are shown in Figure 4.13. The slag volume under the foam in these figures has been divided into two parts: the upper one, termed the “foaming layer”, had a thickness of the order of 3-6 mm corresponding to 25 – 50 % of the of the total slag depth. The thickness of the foaming layer was found in the present experiments to be dependent on the depth of immersion of the carbonate particles into the slag. The second layer was found to be beneath the upper layer, extending down to the crucible bottom. These two layers are also marked in Figure 4.13.
According to the structural classification of slag foams, as presented by earlier workers [2], the foaming layer can be attributed to “non-drained spherical-bubble foam” and situated between bulk liquid and polyhedral drained foam. In the current work, the foaming layer is considered to have uniform temperature in a view of the strong stirring. The slag bottom layer functions as the heat transfer medium between crucible bottom as well as the sides and the foaming layer due to the temperature gradient. The dimensionless Rayleigh number, calculated for the bottom layer in the present experimental system is in the range of 1000-7000, which shows that the convection heat transfer in slag doesn’t play significant role [35].

In the present work, an attempt was made to describe the foaming phenomenon by the model approach, developed by the present author. In the model (termed here as “shell” model), the rate of the foaming reaction is determined by the rate of heat transfer between foaming layer and decomposition reaction front position within a granule of limestone. According to Hills [36], the heat transfer is the major factor, affecting the decomposition of limestone and such a model seems to be more suitable for the foaming descriptions.

The lowering of the average temperature of the foaming layer for a certain time interval is governed by the balance of energy required for carbonate decomposition and delivered from the bottom layer and crucible walls by heat transfer and is calculated as:

$$\Delta T = \frac{(Q_{\text{dec}} - Q_{\text{in}})}{C_p \rho V f}.$$  \hspace{1cm} (4.16)
where $C_{p2}$ – slag heat capacity, J/(kg·K); $\rho_2$ – slag density, kg/m$^3$; $V_{f.l.}$ – the volume of foaming layer, m$^3$; $Q_{\text{dec}}$ and $Q_u$ – the amounts of energy consumed for carbonate decomposition and transferred from the bottom layer respectively, which can be calculated as:

$$Q_u = \frac{S}{h}K_2(T_{bw} - T_{f.l.})(t_2 - t_1),$$

(4.17)

where $S$ – the slag surface area, m$^2$; $K_2$ – slag thermal conductivity, W/m·K; $T_{bw}$ – slag temperature at the bottom and at the walls, K; $t_2$-$t_1$ – time interval duration, s; $h$ – the depth of bottom layer, m. Since the contact area between foaming layer and crucible walls is smaller than with bulk slag, the heat transfer from the crucible walls to foaming layer was neglected in order to simplify the calculations.

Because of fast decomposition process, it is assumed that CaO remained undissolved and the thickness of CaO shell increases as the reaction proceeds. The temperature of limestone decomposition is constant and equal to 1171 K at the atmospheric pressure.

Slag heat conductivity should be in the range of 0.15-0.5 W/(m·K) for the systems, with compositions close to those chosen in present experiments [25]. The heat conductivity value of 0.15 W/(m·K) was found to give a good agreement in describing experimental temperature profiles, and, thus, was chosen for the model.

The heat transfer from bulk slag to spherical surface of particle can be calculated [35]:

$$Q_{sl} = 4\pi R K_2(T_{f.l.} - T_{surf})(t_2 - t_1),$$

(4.18)

where $T_{surf}$ – the surface temperature of CaO/CaCO$_3$ granule, K; $R$ – sphere diameter, m.

The heat transfer within the CaO shell can be described as [35]:

$$Q_{sp} = \frac{4\pi K_{CaO}^{eff} (T_{surf} - T_{dec})(t_2 - t_1)}{r} \left( \frac{1}{r} - \frac{1}{R} \right),$$

(4.19)

The influence of CaO porosity on the effective thermal conductivity ($K_{CaO}^{eff}$) can be estimated by using Maxwell-Eucken expression [37]:

$$K_{CaO}^{eff} = K_{CaO} \frac{1 - p}{1 + \beta p},$$

(4.20)
where \( P \) — estimated porosity (which is admittedly approximate); \( \beta \) — a pore shape factor, which was taken as \( 2/3 \) for randomly dispersed cylindrical pores. The porosity was calculated as the ratio:

\[
p = \frac{\rho_b - \rho_e}{\rho_b},
\]

(4.21)

where \( \rho_b \) — bulk density of the material; \( \rho_e \) — density, determined experimentally. It was found that the limestone samples didn’t change their size after decomposition; hence the density of CaO layer was calculated from measured density of limestone considering no volume change during decomposition. Initial parameters used for modeling are presented in Table 4.9. Assuming that \( Q_{sl} = Q_{sp} = Q_{dec} \), and that the heat of limestone decomposition \( (Q_{dec}) \) includes both change in reaction enthalpy and substances heating, it is possible to find intermediate temperature \( T_{surf} \) and thus the amount of heat transferred inside the particle for each time interval. The calculations were repeated for each 1 second interval to recalculate the temperature of “foaming layer”, CaO shell thickness and decomposition rates. The sample of limestone was approximated to the spherical particles of the following size distribution fraction, viz. 0.5 mm radius particles – 20 % (by mass), 1.0 mm – 60 %, 1.5 mm – 20 %. The calculations were performed simultaneously for a stated amount of each fraction. The results from the shell model approach is presented in Figure 4.14.

<table>
<thead>
<tr>
<th>Thermophysical parameter</th>
<th>Value</th>
<th>Source</th>
<th>Thermophysical parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag density, kg/m(^3)</td>
<td>3000</td>
<td>[33] ([b])</td>
<td>Thermal conductivity of bulk CaO, W/m-K</td>
<td>0.69</td>
<td>[16]</td>
</tr>
<tr>
<td>Slag heat capacity, J/kg-K</td>
<td>1238.4</td>
<td>TS ([b])</td>
<td>Thermal conductivity of slag, W/m-K</td>
<td>0.15</td>
<td>[17]</td>
</tr>
<tr>
<td>Limestone decomposition energy, kJ/kg</td>
<td>3400</td>
<td>([b])</td>
<td>CaO effective thermal conductivity, W/m-K</td>
<td>0.224([a])</td>
<td></td>
</tr>
<tr>
<td>&quot;Foaming layer&quot; depth, m</td>
<td>6.0 (\times) 10(^{-3})</td>
<td>([a])</td>
<td>Limestone decomposition temperature, K</td>
<td>1171 K</td>
<td>[16]</td>
</tr>
<tr>
<td>Limestone density, kg/m(^3)</td>
<td>2700</td>
<td>([a])</td>
<td>Slag viscosity, Pa-s</td>
<td>0.756</td>
<td>TS ([b])</td>
</tr>
</tbody>
</table>

\([a]\) - values determined either experimentally or estimated directly from experimental data;

\([b]\) - values calculated using known models and available data or Thermoslag © software (TS).

The discontinuities in the curve for the model (Figure 4.14) are caused by combining the results from three fractions of sharply-defined size (0.5, 1.0 and 1.5 mm). In real system the size distribution of particles is continuous which should result in more smooth profile.
Figure 4.14 – Comparison of the superficial gas flowrate changes, calculated by “shell” model (line 1) and experimental foam height changes (line 2)

It was found, by comparison between calculated CO$_2$ flow rate and registered foam height (Figure 4.15), that the foaming index is around 0.37 s for system studied, which is much lower than that predicted from Fruehan model [3] and more close to the values, obtained by Niu et al. for CaCO$_3$ decomposition in borate melt (1.02-1.32 s) [17].

Figure 4.15 – The relation between predicted CO$_2$ flowrate (“shell” model) and measured foam height

This may be expected since Fruehan model is valid for static conditions while the present experiments as well as the results of Niu et al. [17] are under dynamic conditions. These results support the conclusions from [38-39] about limited possibilities of foaming index concept when describing slag foaming produced by chemical reactions.
5. Summary and conclusions

Fe$_2$MoO$_4$ was prepared by using commercial grade materials in inert Ar atmosphere. Thermogravimetry, gas chromatography and high temperature XRD studies of Fe$_2$MoO$_4$ formation showed that the reactions in initial mixture start after 873 K and include at least 2 stages. The first stage can be attributed to the Fe$_2$O$_3$ reduction to form FeO, while the second one can be linked to the reduction of MoO$_3$ to MoO$_2$. The formation of Fe$_2$MoO$_4$ from MoO$_2$ and FeO requires higher temperatures or longer soaking time at 1373 K. The investigations of the direct reduction of the mixture of Fe$_2$MoO$_4$ precursors to metallic phases by adding excess carbon using gas chromatograph analysis showed that the reduction proceeds in 2 steps. During the first one, only CO$_2$ could be detected while CO formation was noticed during the second step of reduction.

The evaporation rate of pure MoO$_3$ was studied by TGA and compared with the evaporation rates from mixtures of MoO$_3$ with CaO, CaCO$_3$, MgO. It was found that MoO$_3$ can be stabilized by mixing with CaO, MgO or CaCO$_3$ and heating the mixtures, which would result in the formation of the respective molybdate. The formation of CaMoO$_4$ from the mixtures of MoO$_3$ with CaO or CaCO$_3$ starts after 773 K (as confirmed by high temperature X-ray diffraction studies) and is completed around 973 K.

The Mo yield by use of three different Mo alloying mixtures (MoO$_3$+C; MoO$_3$+C+FeO$_x$; and MoO$_3$+C+CaO) was tested both in laboratory and industrial experiments. During laboratory experiment, both in 16- and 500-g-scale trials, Fe$_2$MoO$_4$ precursor mixture (MoO$_3$+C+FeO$_x$), showed the Mo yield is up to 98 %, which can be explained by the absence of molybdenium evaporation from this substance.

During industrial trials, it was found that for the Fe$_2$MoO$_4$ precursor mixture (MoO$_3$+C+FeO$_x$), the Mo yield was scattered between 89 % and 98 % depending on the granules size of iron oxide. The highest Mo yield of 97.8 % was achieved only by use of small-sized iron oxide and it is close to the results found during laboratory experiments (98 %). For the mixture of (MoO$_3$+C), the yield was found to be around 93 % both for laboratory and industrial treatment. In the case of the mixture M3 (MoO$_3$+C+CaO), the Mo yield is 92.4 % obtained from industrial trials which is much higher than that obtained from laboratory studies which is only 77 %.
A new crucible design for a single thermocouple thermal analysis was used for studying the heat effect of slag foaming with carbonates addition by following the temperature changes. The method enables the study of the full decomposition inside the slag. The technique was tested in the case of dolomite and limestone decompositions in the temperature range of 1623-1723 K with a slag of the composition: CaO - 31 %; SiO₂ - 31 %; MgO - 7 %; Al₂O₃ - 6 %; FeO - 25 %. The lower temperature of the measurement was limited by poor heat conductivity of the slag, while the upper limit was set by very high speed of the decomposition of the carbonates, which can result in partial slag splashing and/or unreacted carbonate particles blowing out of the crucible.

The heat effects of dolomite and limestone decompositions were determined at 1623 and 1673 K. No influence of sample shape on decomposition energy was found for both limestone and dolomite at 1623 and 1673 K. There is no appreciable influence of carbonate type as well. It was found that the decomposition energies for dolomite and limestone for the studied slag composition are in the range 56-79 % of theoretical values, which is attributed to the energy saving effect of slag foaming.

The kinetics of slag foaming by limestone particles was studied at 1773 K with the aid of X-ray imaging system. A heat transfer model was implemented to describe the decrease in foam height with time on the basis of the lowering of the average temperature and CaO shell formation during decomposition reaction.

The energy impacts for limestone and raw dolomite additions were studied in 100-ton EAF. It was found that, in the case of carbonate addition to liquid steel bath, the heat effects for limestone and dolomite (2255 and 2264 kJ/kg respectively) were 70 % of the theoretical values. Carbonate additions along with scrap charging were found to result in larger energy losses. It was found from the trial heats with dolomite addition to liquid steel bath that the partial substitution of lime with raw dolomite does not lead to the increase in energy consumption.
6. Future work

It is planned to test the influence of the size of iron oxide pieces on the yield of Mo in 5 ton induction furnace at Uddeholms AB, Hagfors, Sweden. After that, the yield of Mo during steel alloying in 60 ton EAF will be tested at the same company.

The reduction of mixture MoO$_3$ and FeO$_x$ by carbon will also be studied. The current results show that two separate steps of mass changes were found during the reduction. It will be interesting to recognize the nature of these steps and discover intermediate products in the process. To achieve these aims, high temperature XRD experiments are planned in Ivan Franko National University (Lviv, Ukraine).
References