

A study on transformation of some transition metal oxides in molten steelmaking slag to magnetically susceptible compounds

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Abstract: Sustainable development of steelmaking requires solving a number of environmental problems. Economically feasible and environmentally friendly recycling of slag wastes is of special concern. Research of the team representing National Metallurgical Academy of Ukraine, Royal Institute of Technology, Carnegie Mellon University and URS Corp revealed a possibility of the controlled phase transformations in the liquid silicate melts followed by formation of the magnetically susceptible compounds. This approach enables selective recovery of metal values from slag. In this paper, the results obtained and further research directions are discussed. A possibility to exploit physical properties of the transition metals, typical for the metallurgical slags (such as Fe, Mn, V and others), and corresponding specific properties of their compounds, such as non-stoichiometry, mixed valency, pseudomorphosis, thermodynamic stability etc, in production of value-added materials from slag wastes is discussed. The results of the studies of thermodynamics and kinetics of oxidation in slags followed by phase transformation with binary, ternary and complex oxides under various physicochemical conditions are discussed in the view of their application for production of the materials with predefined physical properties. Peculiarities of precipitation in slags with various basicities are analysed and demonstrate capacity of the proposed approach in the production of the material with a given structure and size – for example, nano-sized crystals with structure of spinel. The approaches towards industrial realization of the developed method are also discussed.

Keywords: slag, recycling, oxidation, magnetic susceptibility

1. Introduction

Sustainable development of metallurgical industry requires solving a number of environmental problems. Economically feasible and environmentally friendly recycling of slag wastes is of special concern.

Due to various technological reasons and thermodynamic limitations, metallurgical slags besides their main components (CaO, SiO₂, MgO, Al₂O₃ and some others) usually contain metals in an oxidised form, which are commonly thought as losses of the target product.

Slag of blast furnace ironmaking contains minor quantity of this kind of losses (less than 1.5% of FeO), hence no methods of their recovery considered for these slags. In contrast, steelmaking slags usually contain essential quantity of target metals in oxidised form. Main component of such losses is FeO, iron monoxide (wüstite), the quantity of which,

depending upon the technology used, varies 7 to 30%. During production of special and alloyed steel grades, the presence of Mn, V, Cr, Co, Mo and some other metals' oxides in slag can be also significant: e.g. 3-8% MnO, 4-6% V₂O₅, 2-9% Cr₂O₃.

There is no industrially proven solution for the recovery of iron from oxidised form known so far. An approach involving reduction of FeO with application of solid fuel has been proposed [1]; however, its implementation is constrained by unavoidable carbon footprint and large energy consumption. Similarly, no proven technology to recover Mn from the steelmaking slags exists.

More attention is focused on the problem of V recovery from slag, which is determined by much higher added value of the recovered product. Furthermore, a hazardous effect of the high-V slag on human health constrains its application in construction [2]. Existing approaches to recover V from slags such as direct soda roasting, direct acid leaching and slag reduction are summarised by Ye and Kim [3] and essential shortcomings such as environmental problems and large energy consumption are identified.

Recent research of the team involving the authors from the National Metallurgical Academy of Ukraine, the Royal Institute of Technology, the Carnegie Mellon University and URS Corp revealed a possibility of the controlled phase transformations in the liquid silicate melts followed by formation of the magnetically susceptible compounds. This approach creates new opportunities in the development of an innovative method for selective recovery of valuable materials from metallurgical slag wastes. In the current paper, the results obtained are discussed in the view of further research directions in this field and possibility of its technological realisation.

2. Peculiarities of transition metals

It is worth mentioning the fact that the metals indicated as losses above belong to the group of transition metals. Peculiarities of the transition metals' ions, owing to incompletely filled *d* orbitals and low reactivity of unpaired *d* electrons, include such untypical properties as: formation of compounds in many oxidation states, non-stoichiometry, compounds with mixed valence, pseudomorphosis, which result in a variety of physical properties such as different forms of magnetism, catalytic activity, formation of coloured compounds, etc.

The variety of structure and properties depending on oxidation state is demonstrated below with the iron oxides:

- highest oxide Fe₂O₃ (hematite) has rhombohedral crystal system and is a canted antiferromagnetic material;
- magnetite Fe₃O₄ has spinel crystal structure, in which the tetrahedral sublattice is filled by the Fe³⁺ ions while the formal valence of iron on the octahedral sublattice is 2.5; Fe₃O₄ is thus a mixed valence compound [4]; exhibits ferrimagnetic behaviour and has high magnetic susceptibility;
- martite is a hematite pseudomorph after octahedral sublattice of magnetite produced by oxidising;
- maghemite γ Fe₂O₃, an allotropic form of magnetite, has a spinel structure isomorphous to magnetite, chemical composition of hematite and ferrimagnetic properties;

- wüstite (ferrous oxide – FeO) is paramagnetic material; prone to nonstoichiometry, which is usual for transition metals in lower oxidation state due to easy oxidation of Fe²⁺ to Fe³⁺ replacing a certain number of Fe²⁺ with 2/3 of Fe³⁺ ions.

Data on the specific magnetic susceptibility for the listed materials are summarized in Table 1 (the value for quartz is also presented for comparison).

Table 1 Specific magnetic susceptibility of some materials

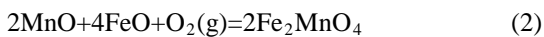
Mineral	$\chi_v \times 10^6$
Magnetite	50 000
Maghemite	25 000
Martite	10 000
Wustite	7 500
Hematite	250
Quartz	10

From the data above one can see that a large variety of properties in the iron oxides may be achieved simply by structural and compositional tuning. In mineral processing, this is used in magnetising roasting technology which is used to convert weakly-magnetic materials to stronger magnetic compounds by transformation of hematite to maghemite under reducing conditions [5]. In case of complex (e.g. Fe-V, Fe-Mn and other) oxides even more versatile properties can be achieved, giving a higher value to the product.

3. Oxidation concept

An oxidation concept was proposed by Semykina [6] and further developed in a team of present authors as a method enabling selective recovery of oxidised iron and manganese values due to transformation of non-magnetic Fe and Mn oxides to magnetic compounds such as Fe₃O₄ and Fe₂MnO₄. Practical realisation of this concept involves following major assumptions:

1) that oxidizing processes in a liquid state can result in the following reactions



2) that ferrites produced in liquid slag will be kept through solidification

3) that separation of the obtained materials from the bulk is possible using magnetic or some other methods.

3.1. Processes in CaO-SiO₂-FeO and CaO-SiO₂-FeO-MnO slag systems

Thermodynamic possibility of phase transformations in the liquid slag leading to the formation of the above mentioned compounds can be seen from the results of Gibbs energy calculations with the help of HSC 4 Chemistry [7]). Fig 1 shows that over 1700 K, FeO can be oxidised to Fe₃O₄ (reaction 1) and its further oxidation to Fe₂O₃ is not thermodynamically possible. Fig 2 also demonstrates that Fe₂MnO₄ can be obtained via reaction 2.

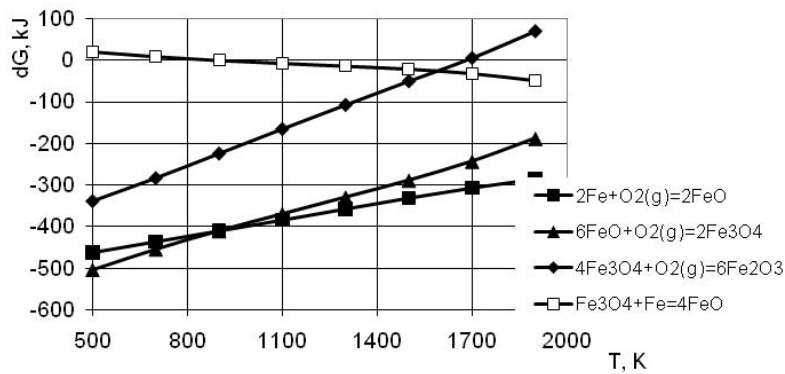


Fig. 1. Gibbs energy for the reactions with iron oxides

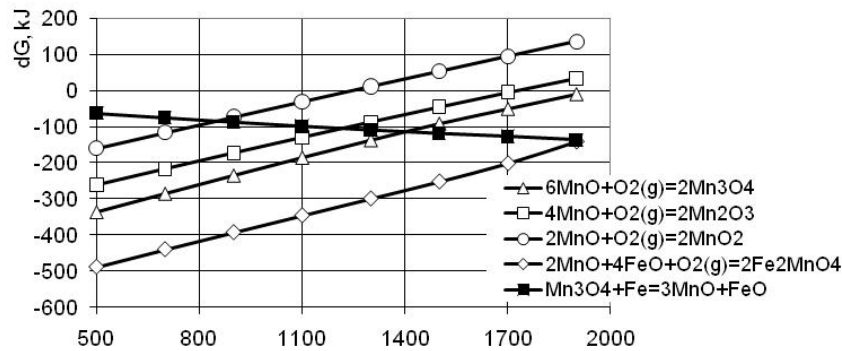


Fig. 2. Gibbs energy for the reactions with manganese and iron oxides

More details should be taken into account with respect to real operation conditions in steelmaking. From the Fig.1 it is possible to see that reaction 1 has higher Gibbs energy above 900 K than reaction of iron oxidising:



Real steelmaking slag usually contains a certain amount of iron droplets. Hence, thermodynamically, oxidation of FeO can start after all metallic iron is oxidized. It is reasonable not to oxidise iron but first to separate iron droplets from liquid slag and then apply oxidizing route. However the method for separation of iron droplets from liquid slag is unknown in practice.

Reaction of “re-reduction” of Fe₃O₄ by iron:



was also taken into account; however its probability under concerned conditions seems minor.

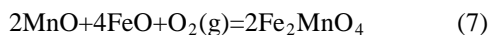
Oxidation of MnO (Fig 2) may proceed through a number of routes, most possibly via the following reaction:



However, in case iron droplets are present in slag and not oxidized prior to MnO oxidizing, produced Mn₃O₄ can be reduced as follows:



These results might be considered as challenges in accomplishing 1st of the above mentioned assumptions. However, in complex FeO and MnO bearing slags very high thermodynamic possibility of obtaining Mn ferrite exists through the following reaction:



Another aspect to be noted is that in the silicate melts, owing to the presence of calcium, silicon and other oxides, much more complex processes occur than those presented in Fig 1 and 2. Thermodynamic equilibria under various oxygen partial pressures for complex silicate slags were modelled using FactSage 6.1 software [8]. In Fig.3, results for a ternary CaO-SiO₂-FeO system demonstrate that crystallisation of oxidised iron in the form of magnetite can be ensured under the oxygen pressure lower than those in air. However, in the case of quaternary CaO-SiO₂-FeO-MnO system, a complex (Fe-Mn) ferrite with the structure of spinel crystalizes in a wide range of oxygen partial pressure. Together with the analysis of oxidation reactions (Fig 1-2), this supports the idea that application of the concerned approach is more reasonable for complex slags containing both Mn and Fe oxides.

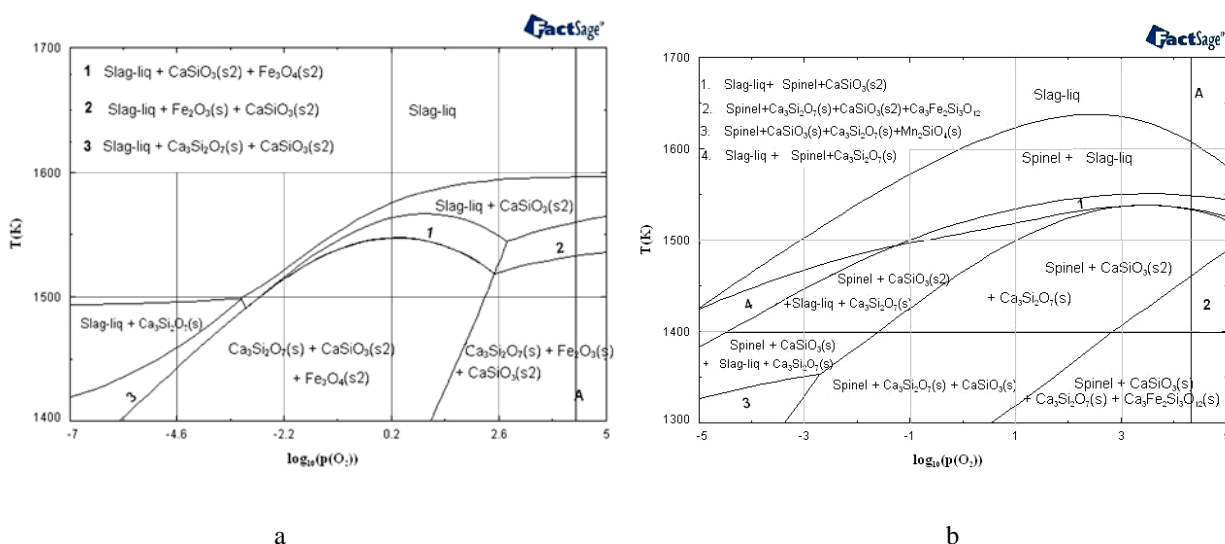


Fig 3. Phase diagrams for: a) ternary CaO-SiO₂-FeO; b) quaternary CaO-SiO₂-FeO-MnO systems. Line marked (A) corresponds to the partial pressure of oxygen in air in Pa.

Oxidation processes in liquid synthetic slags were studied using a derivative thermogravimetry technique showing intensive mass gain due to oxidation in both CaO-SiO₂-FeO and CaO-SiO₂-FeO-MnO. It was found that an oxidation rate achieved in final product can be controlled by the temperature. Effect of slag basicity was also studied and more rapid oxidation for slags with lower basicity was found. Study conducted with application of CSLM (confocal scanning laser microscopy) allowed to observe *in situ* nucleation of crystals driven not by cooling (the experiments were conducted under isothermal conditions) but by oxidation and subsequent phase transformation. More details on this study can be found in our publications [9-12]. Obtained results give no place to doubts about a possibility to transform non-magnetic oxides to materials with high magnetic susceptibility in the laboratory scale. Scale-up to the pilot

conditions might be challenging, taking into account a need for very accurate adjustment of temperature and partial pressure of oxygen.

Phase equilibria presented in Fig.3 reveal that the presence of iron oxide in the solid product does not always ensure that a magnetically susceptible form is produced by oxidising in liquid. Indeed, the XRD patterns (Fig.4) for the samples obtained after TGA experiments by treatment of CaO-SiO₂-FeO slag under oxidizing conditions and subsequent in-furnace cooling demonstrate that the solidified product contains Fe₂O₃, which corresponds to the results of thermodynamic modelling and is undesirable in the view of the recovery concept concerned. In contrast, for the samples obtained by similar procedure in CaO-SiO₂-FeO-MnO slag system XRD results demonstrate the essential presence of Fe₃O₄ and Fe₂MnO₄ with no Fe₂O₃ (Fig 5).

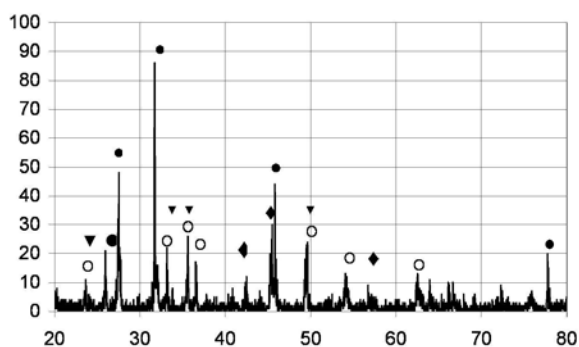


Fig 4 XRD pattern for slag 37.5%CaO, 37.5%SiO₂, 25%FeO after oxidising at 1673 K: o = Fe₂O₃; ◆ = Fe₃O₄; ● = CaSiO₃; ▼ = Ca₂Fe₂O₅

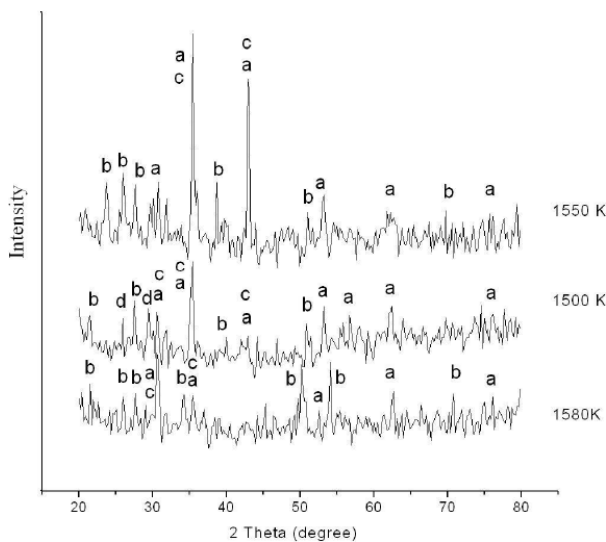
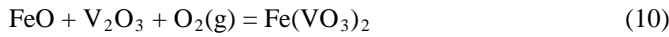
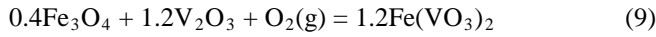


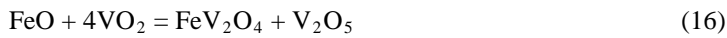
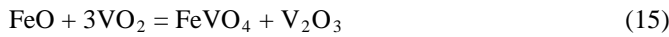
Fig 5. The XRD pattern for slag 21%CaO, 34%SiO₂, 30%FeO, 15%MnO after oxidising: a – Fe₂MnO₄; b- CaSiO₃; c-Fe₃O₄; d- Ca₃Si₂O₇.

3.2. Processes in V-bearing slag

Thermodynamic analysis reveals a possibility of formation of complex Fe-V compounds by oxidation in V-bearing slags. The following reactions have negative Gibbs energy under conditions concerned:



For the following reactions only positive Gibbs energy values were obtained:



Therefore, some of the reactions involving VO_2 and V_2O_3 yielding vanadium ferrites are thermodynamically allowed, in contrast to the reactions involving V_2O_5 .

Simultaneous analysis of the results¹ of modelling phase equilibria in Fe-O and in V-O systems shows (Fig 6) that the conditions when such couples as for example FeO and V_2O_3 , or Fe_3O_4 and VO_2 are present in a liquid state can be created under slightly oxidising atmosphere. Hence there is a possibility of a controlled phase transformation involving e.g. reactions 8 or 10 and leading to the formation of $\text{Fe}(\text{VO}_3)_2$.

A thermodynamic route enabling retaining of the complex Fe-V oxides produced through cooling and solidification remains unknown and requires further investigation. However, a possibility to experimentally obtain complex Fe-V oxides under low partial pressure of oxygen (in Ar atmosphere) was confirmed [13] and XRD pattern of produced material is represented in Fig 7. This result is optimistic in terms of the development of a method for treatment of the V-bearing slags and their subsequent selective utilisation.

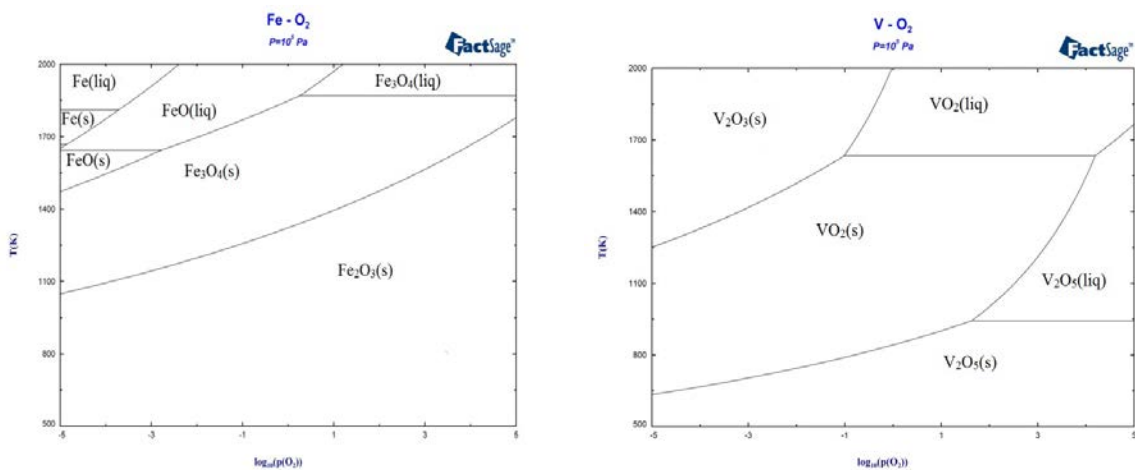


Fig. 6. Phase stability diagram for the Fe-O and V-O systems

¹ FactSage calculations and experimental studies concerning V-bearing slags presented in this paper were performed by Iryna Dzhebian, MSc student of the National Metallurgical Academy of Ukraine

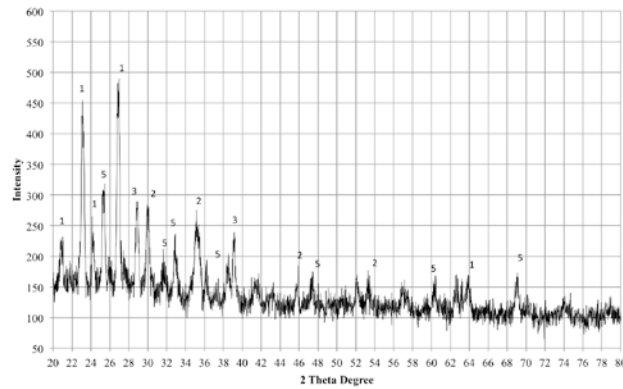


Fig. 7. XRD pattern for slag 46.5%CaO, 38.5%SiO₂, 10%FeO, 5%V₂O₅ after oxidising in Ar ($P_{O_2} = 10^{-1}$ - 10^{-2} Pa) at 1773 K: 1 - FeVO₄, 2- Fe₂VO₄, 3 - FeV₂O₄, 5- CaSiO₃, Ca₂SiO₄

4. Recovery of the obtained compounds from slag

4.1. Separation from solidified product

Recovery of the obtained compounds from the slag bulk using magnetic separation is possible under following conditions:

- that the target phase can be detached from the silicate matrix by grinding;
- that the difference in magnetic susceptibility allows for efficient concentration of the target phase with acceptable energy consumption.

CSLM study revealed that the target material nucleates in a form of crystals sized as 50 nm and larger and the size can be controlled by changing the slag basicity. A possibility of their separation was not studied so far. From mineral processing, it is well known that the larger the grains or crystal forms of target material are, the simpler the processing method and the lower energy consumption are. On the other hand, a nano-size may give an added value to the product (e.g. for electro-technical applications) which could make higher consumption of energy affordable. Therefore an optimal size is seen as a trade-off solution and requires further investigation. However, it should be noted that magnetic separation even of submicron and especially nano-sized particles is a very complex technological problem.

4.2. Separation from liquid state

As alternative to magnetic separation, a novel method to control the movement of solid particles suspended in liquid using electromagnetic buoyancy force (EBF) was studied on the cold model. Such a force can be created in the crossed electric and magnetic fields and affects even non-magnetic particles. Hence, despite the fact that the temperature of liquid slag is obviously over Curie point for the materials concerned, the controlled movement of suspended solid phase towards cathode or anode can be ensured. Theoretical background for the EBF and a method of cold modelling are explained in detail in our earlier publication [14]. The results obtained are very promising in terms of a possibility to separate the target compounds prior to solidification which has the following advantages:

- unwanted phase transformations can be avoided;
- possible target compounds with low magnetic susceptibility can be separated;
- a need for grinding of the whole the slag produced can be avoided.

Verification of the proposed method on hot model under laboratory conditions is planned in the future. However a major barrier to be tackled is a possibility to up-scale the laboratory installation. In particular to insure that in a vessel with 0.1 m diameter a particle with the size of 0.05 mm moves with a velocity of 2.5 mm/min, 10 Tesla magnetic field must be created, which requires application of very large transformers and powerful electric winding around the vessel with liquid slag, which may appear too expensive and difficult to fit to the existing industry spatial limits. Application of superconductors may solve the problem, however this technology has own barriers to overcome on the way to industry. Another possible approach for separation owes to the fact that - as revealed in CSLM experiments – ferrites precipitate on the slag surface. Skimming of the upper slag layer and its subsequent quenching in water will produce a slurry with high concentration of the ferrites subjected to further treatment.

5. Conclusions

1. The method of transformation – the non-magnetic compounds of transition metals to the ferrites with high magnetic susceptibility involving oxidation – is a promising method enabling efficient selective utilisation of steelmaking slags.
2. Magnetically susceptible compounds, nucleated in liquid slag can undergo unwanted phases transformation, which might be tackled using such tools as temperature regime, tailored gas atmosphere and slag compositions
3. Complex oxides such as manganese ferrite demonstrate higher stability through the solidification processes compared to magnetite. Hence the proposed concept might be applied to simultaneous treatment of slags produced in different industries (e.g. steelmaking and ferroalloys) in order to maximise the yield of the target product recovered from the waste.
4. Separation method for the solid product requires further study involving synergy of efforts in such issues as particle size control, grinding and magnetic separation. A method of separation from the liquid slag based on electromagnetic buoyancy force is seen as promising alternative.

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