Perspectives of Chemical Metallurgy Fundamentals in Slag Innovation

Sanghoon Lee[1] *and Il Sohn*[2]

1.Research Professor, Yonsei University, Seoul 03722. Email:slag@yonsei.ac.kr
2.Professor, Yonsei University, Seoul 03722. Email:ilsohn@yonsei.ac.kr

Keywords: Slags; Chemical Thermodynamics; Kinetics; Nucleation and growth; Phase distribution;

ABSTRACT

The ferrous and non-ferrous metallurgical industries have been utilizing slags, fluxes and mattes for process optimization and quality improvements at high temperatures. Understanding the fundamentals of the thermodynamics and kinetics of chemical metallurgy regarding slags, fluxes and mattes has been essential to the technological developments of these optimization and improvements. This work will discuss how these fundamentals have been studied in the reactions involved and implemented in the ferrous industry from primary refining to continuous casting. In particular, the chemical driving forces that allow these reactions to take place and the limitations of the kinetics that require optimization to enhance the reactions. In addition, the future research direction for slag technology innovation and the role of these fundamentals will also be described.

INTRODUCTION

Ferrous metals including iron and steel are widely used for structural materials imbedded in nearly all industry sectors including construction, shipbuilding, transportation and many others. Non-ferrous metals are typically added into the basic materials of the ferrous metals to improve the various physical and chemical properties.

According to the World Steel Association (World Steel Association, 2023), approximately 1.9 BT of crude steel was produced. For non-ferrous metals, the US Geological Survey notes that world aluminium output was 69 MT (US Geological Survey, 2023) and publications from the Government of Canada indicates global refined copper production to be 25 MT. Depending on the metals processing method, large amounts of slags and mattes are produced. Global slag generation from these processes have been estimated to be approximately 500 MT within the ferrous industry. (Yang et al., 2022)

The critical role of slags and mattes in chemical metallurgy cannot be overstated in terms of their importance to the final product quality. Although the humble beginnings of the slag and matte may have started out in part as gangue components in the raw materials, the product quality, energy benefits and protection from the environment with optimized design have become essential for process engineering. For slags in ferrous metallurgy, optimized slags have the ability to refine unwanted elements in the molten metal including sulphur, phosphorus, nitrogen, hydrogen and other elements. When a slag covers the molten metal, it acts as a barrier to the outside environment minimizing the infiltration of dissolved gaseous elements into the molten metal and can also act as a thermal barrier for increased insulation of the molten metal. For mattes in nonferrous metallurgy, optimized mattes can increase the recovery of the non-ferrous element and improve the separation efficiency of the oxide slags and also increase the purity of the target element. The typical sulphide mattes used for primary copper smelting operations and the slags that are formed during smelting of the concentrates comprised of oxy-sulphide minerals require process optimization to ensure greater recovery of copper is possible, while maintaining greater purity with less ferrous impurities in the matte. With higher concentrations of Cu can be achieved in the matte, it can be sent to the converter for sulphur removal and subsequent blister Cu production.

The fundamentals that control the role in slags and mattes are based on thermodynamic and kinetic principles, which have been widely studied in chemical metallurgy. This review looks at some of the fundamentals of ferrous and non-ferrous chemical metallurgy that have been applied to ensure greater process efficiency and product quality.

THERMODYNAMIC FUNDAMENTALS

1. Slag capacities in steelmaking and refining

Slag capacity in steelmaking and refining is the ability of a slag to absorb and retain various impurities and elements during high temperature metallurgical processes. Several critical factors affect slag capacity, which in turn interacts with the chemical and physical properties of the slag. These factors have been widely studied and includes the slag chemical composition, temperature, and oxygen partial pressure.

Slags can typically be comprised of SiO_2, Al_2O_3, CaO, MgO, and FeO, which can influence the thermophysical properties of the slag including the viscosity and the chemical potential of the slag including the basicity, which have been known to directly impact the absorption and retainment of impurities from molten steel. Temperatures provide the thermal energy to the system for reaction and the kinetic energy of the bondings within the ionic slag melts to form new bonds. Depending on the exothermic or endothermic reactions between the slag and metal, reactions can be hindered or accelerated. Temperatures can also affect the viscosity and fluidity of slags, where higher temperatures lower the viscosity and increase the fluidity.

Oxygen partial pressure or oxygen potential of the system influences the redox reactions occurring at the slag-metal interface, where the impurities of sulphur and phosphorus can be exchanged. Low oxygen potentials or reducing conditions can promote the removal of certain impurities such as sulphur into the slag as sulphides, while high oxygen potentials or oxidizing conditions may facilitate the removal of certain impurities such as phosphorus into the slag by forming stable oxide phases as phosphates. While not typical, slag viscosities and phase equilibria can be altered under high pressures, affecting the capacity of a slag to absorb impurities.

Basicity, which refers to the chemical potential of the free oxygen anions, is difficult to directly measure, but is one of the critical parameters determining the capacity of the ionic slag to remove impurities from metals during metallurgical processing. Thus, an indirect measure of the slag basicity was warranted and the Vee ratio defined as the mass ratio of basic oxides (e.g., CaO, MgO) to acidic oxides (e.g., SiO_2, Al_2O_3) in the slag composition was utilized. The basicity of an ionic slag influences both the chemical and physical properties, including the viscosity, fluidity, and slag capacity to absorb and retain impurities. Optimal slag basicity through slag composition design is often crucial for effective impurity removal and slag performance. The adage "Take care of the slag, and the steel will take care of itself" emphasizes the importance of managing the slag effectively in metallurgical processes to ensure the production of high-quality steel.

Considering the aforementioned slag capacity, two key impurities are closely controlled in the steelmaking operations, which include sulphur and phosphorus corresponding to the sulphide and phosphate slag capacities respectively.

Desulfurization of steels typically involves the transfer of dissolved sulphur from the metal into the slag phase. The most common reaction under steelmaking conditions is the formation of calcium sulphide (CaS), when sulphur reacts with calcium oxide (CaO) in the slag, as expressed by reaction (1). The corresponding ionic reaction is express as reaction (2) and the subsequent sulphide capacity under reducing conditions is expressed by equation (3). Depending on the slag composition, the activities of the reactants and products can be significantly modified. Thus, depending on the impurities existing in the steel, the activity of dissolved S can affect the reaction and the components such as Al_2O_3 or SiO_2 in the slag can also affect the activity of the CaO in the slag, which can inherently affect the S transfer to the slag phase.

$$\mathrm{CaO(slag)+S(metal)\rightarrow CaS(slag)+1/2O_2(g)} \qquad [1]$$

$$\mathrm{O^{2-}(slag)+S(metal)\rightarrow S^{2-}(slag)+1/2O_2(g)} \qquad [2]$$

$$C_{S^{2-}} = (\%S) \times \left\{\frac{P_{O_2}}{a_S}\right\}^{1/2} = K_2 \times \frac{a_{O^{2-}}}{f_{S^{2-}}} \qquad [3]$$

According to Figure 1(a) and 1(b), the sulphide capacities according to the Vee ratio (corresponding to the basicity) and the activity of FeO are shown. It is clearly evident that the sulphide capacities for these systems follow the expected thermodynamic interpretations and a slope of unity corresponding to equation (3) is shown. Similar results have been identified for dephosphorization with a slope of 1.5.

In Figure 2, the temperature dependence of the slag capacities are provided. Unlike the basicity, the sulphide and phosphate capacity show opposite trends with the temperature dependence. Higher temperatures are favourable for the sulphide capacity, but lower temperatures are favoured for the phosphate capacity. Dephosphorization is the process of transferring the dissolved phosphorus in the molten metal to the slag phase resulting in the desired product specifications. Considering phosphorus removal in steelmaking occurs under a high oxygen partial pressure, the typical main reaction corresponds to the formation of a phosphate phase in the slag. Phosphorus reacts with CaO in oxidizing conditions to form calcium phosphate ($Ca_3(PO_4)_2$), as described in reaction (4). The reaction in ionic form can be expressed as reaction (5). Accordingly, under oxidizing conditions of steelmaking operations, the phosphate capacity can be expressed by equation (6).

$$3/2CaO(slag)+P(metal)+5/4O_2(g)\rightarrow 1/2Ca_3(PO_4)_2(slag) \qquad [4]$$

$$3/2O^{2-}(slag)+P(metal)+5/4O_2(g)\rightarrow PO_4^{3-}(slag) \qquad [5]$$

$$C_{PO_4{}^{3-}} = (\%PO_4^{3-}) \times \frac{1}{a_P \times P_{O_2}^{1/2}} = K_5 \times \frac{a_{O^{2-}}^{3/2}}{f_{PO_4^{3-}}} \qquad [6]$$

Similar to sulphur, the slag capacity for phosphoros removal from the metal to the slag depends on various factors including temperature, slag composition, and activities of the reactants and products. It should be noted that under a fixed temperature and oxygen partial pressure, the slag capacities are determined according to the slag system.

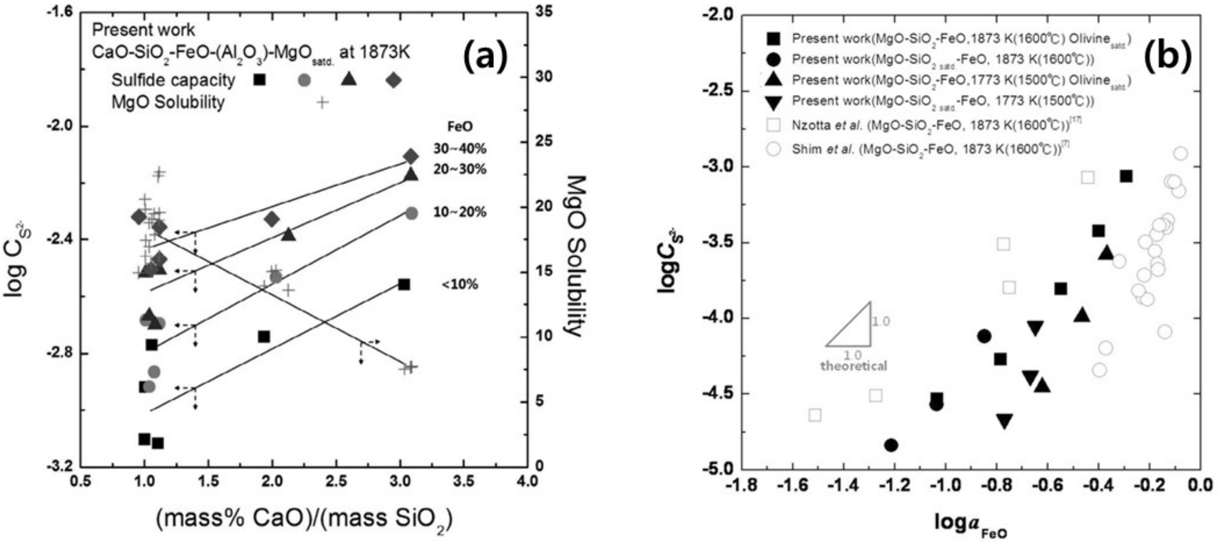

Figure 1. Sulphide capacities of various slag systems as a function of (a) Vee ratio (apparent basicity) (Park and Min, 2016) and (b) logarithm of the FeO activity (Kim et al., 2014)

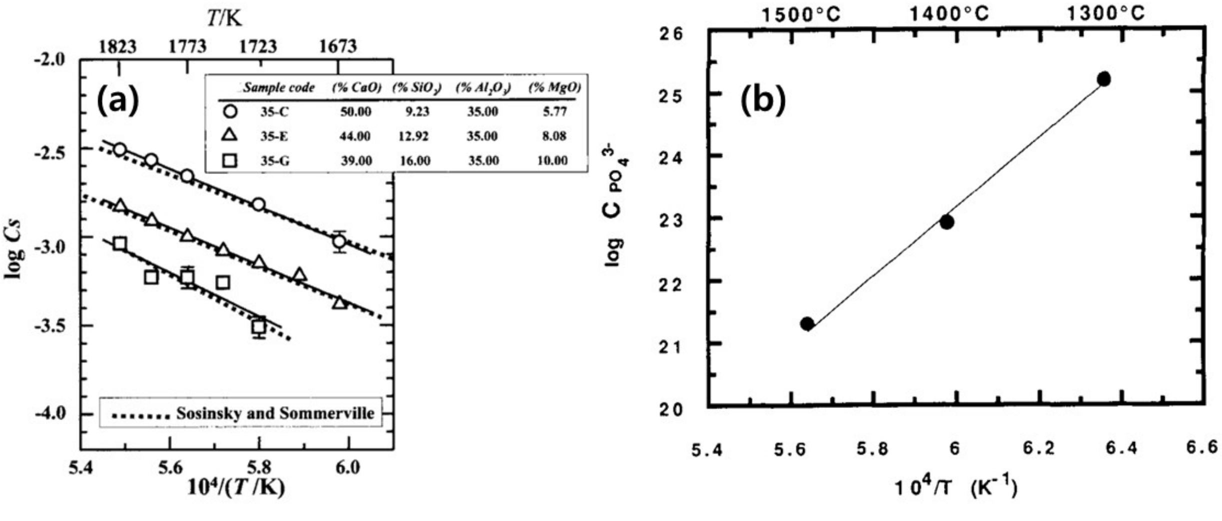

Figure 2. (a) Sulphide capacity and (b) Phosphate capacity as a function of temperature (Nassaralla and Fruehan, 1992)

Overall, the thermodynamics of desulfurization and dephosphorization in slags involve complex interactions between the metal and slag phases, as well as the equilibrium between different chemical species. Understanding these fundamental thermodynamic principles is crucial to optimize steelmaking processes and achieving the levels of S and P removal into the designed slags for steel quality.

2. Matte optimization in non-ferrous metallurgy

Beyond ferrous smelting operations, non-ferrous metallurgy is also a field for chemical metallurgists to make a significant impact on not only the industry, but also the environment considering the significant amount of emissions involved with smelting non-ferrous metals with relatively small concentrations of the product. Unlike ferrous raw materials, non-ferrous raw materials contains typically less than 5 mass pct. of the target metals. Copper is one of the widely used non-ferrous metals that is critical to the electrification of the society. Copper smelting involves various processing stages, including matte production, converting, and refining. Matte, a sulphide-rich intermediate product before the production of blister copper after converting, plays a critical role in determining the efficiency and quality of copper extraction. Significant challenges are associated with matte optimization in copper smelting, which can enhance process efficiency, reduce environmental impact, and improve product quality. Key optimization parameters include flux addition, matte grading, and slag designing. These optimization factors can maximize copper recovery and minimize energy consumption and emissions, ultimately contributing to sustainable copper processing and production.

Matte optimization is challenged by the complexity of sulphide ore composition, feed variability, and impurities such as iron, sulphur, and arsenic. Blending different ore types, adjusting the sulphur-to-iron ratio, and flux additions assists in matte composition optimization and minimize impurities.

Fluxes play a crucial role in copper smelting by facilitating slag formation, promoting metal separation, and controlling impurity levels. Optimizing flux addition rates and compositions improves matte quality, reduces slag viscosity, and enhances metal recovery. Adjusting silica-to-alumina ratio, controlling slag basicity, and minimizing iron oxide content can improve slag fluidity, reduce matte losses, and enhance overall process performance. Silica is a primary flux used in copper smelting to facilitate a liquid slag phase. It helps lower the melting point of the slag, promotes the dissolution of gangue minerals, and improves slag fluidity. Limestone is commonly added as a flux to neutralize acidic impurities such as S and As to form CaS and $Ca_3(AsO_4)_2$, which are then incorporated into the slag phase. Fayalite (Fe_2SiO_4) is a by-product of copper smelting and often recycled, which contribute to the formation of a stable slag phase, absorbing excess sulphur, and assists in controlling the slag viscosity. As described from reactions (7) and (8), copper smelting from sulphide ores is a stepwise oxidation of iron, where the oxygen activity increases resulting in blister copper production. (Taskinen et al., 2019)

$$[CuFeS_2]+ 1x/2O_2(g)\rightarrow[(Cu, Fe_{(1-x)/2})_2S]+x(FeO)+SO_2(g) \qquad [7]$$

$$[Cu_2S]+O_2(g) \rightarrow 2Cu+ SO_2(g) \qquad [8]$$

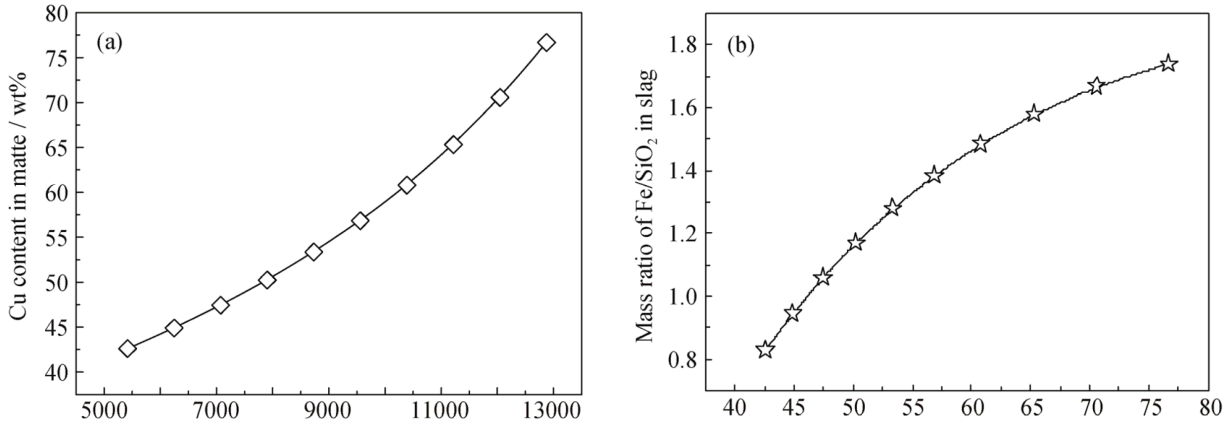

Figure 3. (a) Cu content in matte as a function of oxygen and (b) relationship between the Fe/SiO_2 ratio to the Cu content in matte (Wang et al., 2019)

According to the results shown in Figure 3(a) and 3(b), the Cu content in the matte can be significantly affected by the amount of oxygen activity in the reactor and the subsequent Fe/SiO_2 slag formed during processing. It is generally known that the chemical dissolution affecting Cu loss can be of two possible types: oxidic and sulphidic. However, it is also known that when the grade of matte exceeds 60%, it is influenced by oxidic copper dissolution (Cornejo Mardones, K., 2020). Therefore, higher flow rates, which correspond to higher oxygen potential and activity can increase the Cu content in the matte. However, excessive oxygen injection can not only oxidize the Fe in the chalcopyrite raw material, but can also oxidize the Cu into the slag phase resulting in lower recovery of Cu. As the Fe oxidizes into the slag phase, there are some amounts of SiO_2 fluxing required to optimize the Cu content in the matte. As can be seen in Figure 3(b), higher grade Cu mattes can be obtained with Fe/SiO_2 reaching the ratios beyond 1.6. However, this needs to be balanced since higher oxygen potentials can lead to the formation of Fe_3O_4 in the slag phase, which can increase the melting point of the slag and reduce fluidity and also the separation between matte and slag phase during matte smelting and separation. An optimal Fe/SiO_2 ratio seem to be near the low temperature fayalite phase formation region and thus operations typically would target the slag composition to be in this range.

3. Thermophysical properties of slags and mattes

The thermophysical properties of slags and mattes play a significant role in determining their capacity to interact with molten metal and effectively absorb impurities. These properties influence the behaviour of slags during metallurgical processes, affecting their viscosity, thermal conductivity, heat capacity, and other characteristics.

Viscosity affects fluid flow behaviour and retention of the impurities in slags. Highly viscous slags can impede mass transfer kinetically reducing the slag capacity. This reduced mobility can hinder the absorption of impurities by the slag, limiting its capacity to remove contaminants from the metal. Lower viscosity enhances slag-fluid metal interactions, promoting impurity removal. The viscosity of slag is influenced by temperature, chemical composition, and phase composition. In addition, slags with high viscosity tend to have slower settling rates, prolonging the time required for slag-metal separation. Higher viscosities can also hinder convective heat transfer within the slag, leading to temperature gradients and non-uniform heating. Thus, optimizing slag viscosity is essential for enhancing the slag capacity and improving the efficiency of impurity removal and other desired functions in metal production.

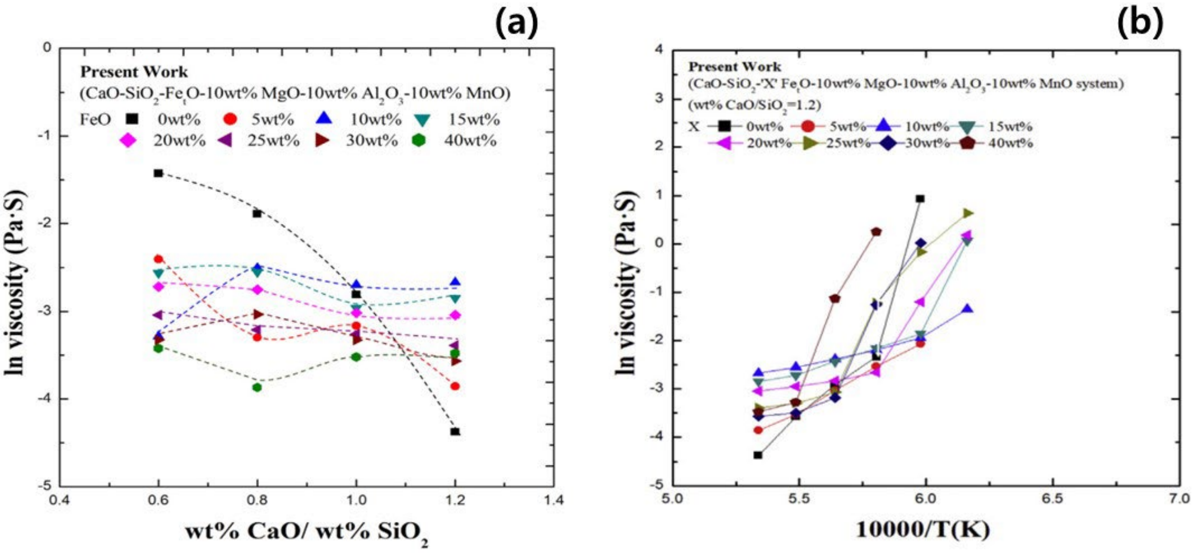

Figure 4. Natural logarithm of the viscosity (Choi et al., 2021) as a function of (a) Vee ratio and (b) temperature

Slags and mattes with higher thermal conductivity can efficiently transfer heat from the surrounding environment, influencing temperature distributions within the system. Temperature gradients affect reaction kinetics and phase equilibria, consequently impacting the slag capacity. Like many of the thermophysical properties of slags and mattes, the thermal conductivity of slag is also influenced by its chemical composition, phase fractions, and temperature.

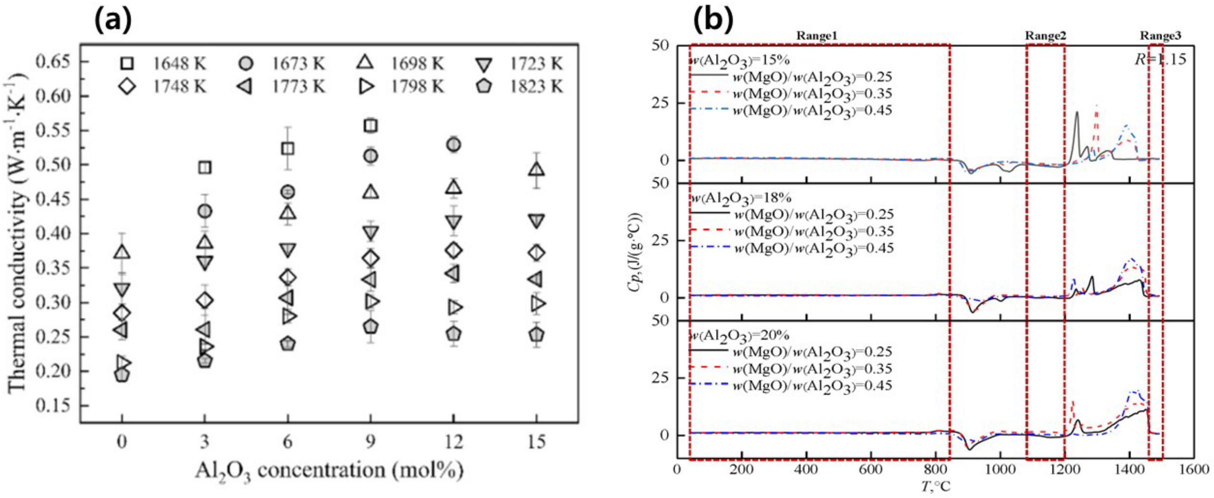

Figure 5. (a) Thermal conductivity of slags as a function of Al_2O_3 content (Yang et al., 2022) and (b) Specific heat capacities of slags as a function of temperature and composition (Zheng et al., 2021)

Slags and mattes with higher specific heat capacity can absorb more heat energy before significant temperature changes can be observed, which impact the energy needs of a reacting system in metallurgical processes. The heat capacity also depends on its chemical composition, phase fraction and temperature.

Understanding and controlling these thermophysical properties are essential for optimizing metallurgical processes using slags and mattes. Slag and matte compositions and process conditions are often manipulated to achieve desired thermophysical properties and improve process performance.

SUMMARY

This review looks briefly at the fundamental thermodynamics and thermophysical properties of slags and mattes for chemical metallurgy. Understanding the theory behind the various reactions and controlling the fundamental chemical potential allows the process engineer to achieve metals production at a more efficient and environmentally optimal way.

ACKNOWLEDGEMENTS

This work was supported by the Technology Innovation Program (Commercialization and development of new design on turbulent high temperature melting furnace (2000 tony pilot scale) and separation and (or) recovery of valuable metals from end of the xEV (ESS) battery pack) (20011183) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

REFERENCES

Joon Sung Choi, Tae Jun Park, Dong Joon Min, and Il Sohn, Viscous behavior of high-Fe_tO-bearing slag systems in relation to their polymeric structural units. Journal of Materials Research and Technology, 2021, Volume 15, 1382-1394

Ki Deok Kim, Wan Wook Huh, and Dong Joon Min, Effect of FeO and CaO on the Sulfide Capacity of the Ferronickel Smelting Slag, Metall. Mater. Trans. B, 2014, Volume 45B, 889

Government of Canada, Natural Resources, Copper facts, https://natural-resources.canada.ca/our-natural-resources/minerals-mining/mining-data-statistics-and-analysis/minerals-metals-facts/copper-facts/20506, Accessed 2024.02.01

C. Nassaralla and R.J. Fruehan, Phosphate Capacity of $CaO-Al_20_3$ Slags Containing CaF_2, BaO, Li_20, or Na_20, Metall. Trans. B, 1992, Volume 23B, 117

Youngjoo Park and Dong Joon Min, Sulfide Capacity of CaO-SiO2-FeO-Al2O3-MgOsatd. Slag, ISIJ Int., 2016, Volume 56, 520-526

Pekka Taskinen, Guven Akdogan, Ilkka Kojo, Markku Lahtinen and Ari Jokilaakso, Matte converting in copper smelting, Mineral Processing and Extractive Metallurgy, 2019, Volume 128, 58-73

U.S. Geological Survey, Adam M. Merrill, Aluminum, 2023

Qin-meng Wang, Song-song Wang, Miao Tian, Ding-xuan Tang, Qing-hua Tian, and Xue-yi Guo, Relationship between copper content of slag and matte in the SKS copper smelting process, International Journal of Minerals, Metallurgy and Materials, 2019, Volume 26, 301

World Steel Association, World Steel in Figures 2023, 2023

Jian Yang, Felix Firsbach, and Il Sohn, Pyrometallurgical processing of ferrous slag “co-product” zero waste full utilization: A critical review, Resources, Conservation and Recycling, 2022a, Volume 178, 106021

Jian Yang, Zhe Wang, and Il Sohn, Topological understanding of thermal conductivity in synthetic slag melts for energy recovery: An experimental and molecular dynamic simulation study, Acta Materialia, 2022b, Volume 234, 118014

Haiyan Zheng, Lisheng Liang, Jinlei Du, Shifa Zhou, Xin Jiang, Qiangjian Gao, and Fengman Shen, Mineral Transform and Specific Heat Capacity Characterization of Blast Furnace Slag with High Al_2O_3 in Heating Process, Steel Research Int., 2021, Volume 92, 2000448

Cornejo Mardones, K., Control of copper loss in flash smelting slags, Master’s Thesis, School of Mechanical and Mining Engineering, The University of Queensland, 2020