Evaluation of Thermal Conductivities of Molten SiO_2-Al_2O_3-CaO Slags

K Tang[1], *M Zhu*[2], *J You*[3], *X Ma*[4] *and G Tranell*[5]

1. Senior Scientist, SINTEF AS, Trondheim N-7436, Norway. Email: kai.tang@sintef.no
2. Post-doc Researcher, Norwegian University of Science and Technology, Trondheim N-7491, Norway. Email: mengyi.zhu@ntnu.no
3. Professor, Shanghai University, Shanghai 200444, China. Email: jlyou@staff.shu.edu.cn
4. Senior Scientist, SINTEF AS, Oslo N-0373, Norway. Email: xiang.ma@sintef.no
5. Professor, Norwegian University of Science and Technology, Trondheim N-7491, Norway. Email: gabriella.tranell@ntnu.no

Keywords: thermal conductivity, molten SiO_2-Al_2O_3-CaO slag, silicate tetrahedron, machine learning, deep neural network

ABSTRACT

The thermal conductivity of slag is critical for the efficiency of high temperature metallurgical processes such as the smelting reduction of ferroalloys, the ladle refining, and the continuous casting mold flux in steelmaking. Experimental determination of slag's thermal conductivity is fraught with challenges, as seen in yielding data for the SiO_2-Al_2O_3-CaO system that are often inconsistent and widely dispersed. In molten slags of this system, thermal transport occurs via phonons within the network structure. To quantitatively describe thermal conductivity based on the microstructure, high-temperature Raman spectroscopy was employed to measure the silicate tetrahedra Q_i (i = 0,1,2,3), with Q_4 species inferred from mass balance. This study also integrated molecular dynamics simulations to provide a fundamental understanding of the microstructure units distributions. Machine learning algorithms, especially deep neural networks, were applied to establish the relationship between slag composition and the configuration of tetrahedra. The thermal conductivities were then connected with silicate tetrahedra Q_i using an Arrhenius-type formalism. This study sets the stage for extending our findings to more complex, multicomponent slags, enhancing their practical application in industrial processes.

INTRODUCTION

The thermophysical properties of molten slags, such as viscosity, conductivity, and diffusivity, are fundamentally linked to their microstructures. Thermal conductivity is crucial in various steelmaking processes including smelting reduction of ferroalloy, ladle slag, and continuous casting mold flux. However, accurately determining the thermal conductivity experimentally for the entire SiO_2-Al_2O_3-CaO slag system poses challenges, caused by inconsistent and scattered data. Consequently, there is lack of robust, physically sound models for mathematically describing the thermal behavior of this molten slag system.

In molten silicate melts, heat conduction occurs through the interplay of molecular movements, particularly the random motion of ions and the vibrational energy within the SiO_4 tetrahedral network, facilitating heat transfer (Wang *et al.*, 2020). This process differs from crystalline solids, where heat transfer is more organized, primarily through lattice vibrations or phonons. The disordered, fluidic nature of molten silicates leads to a less structured heat transfer mode. The melt's structure and composition, influenced by various metal ions and silica content, significantly impact its thermal conductivity. Rising temperatures increase thermal agitation, disrupting regular heat transfer and reducing conductivity. Moreover, the viscosity of molten silicate, indicative of its internal structural complexity (Mills, Yuan and Jones, 2011), is a critical factor. Higher viscosity, associated with more complex network structures, typically results in lower thermal conductivity. Consequently, heat conduction in molten silicates is a dynamic process, intricately linked to the melt’s molecular structure, temperature, and viscosity.

Raman spectroscopy is a powerful tool for studying the structure of molten slag. It can be used to identify the different types of structural units present in the slag, such as SiO_4 tetrahedral Q_i (i=0-4) units. The relative abundance of these different units can provide insights into the degree of polymerization of the molten slag.

In the present work, the microstructure of molten SiO_2-Al_2O_3-CaO slags have been characterized by high-temperature Raman spectroscopy. To visualize the microstructure in these high-temperature silicate melts, molecular dynamics (MD) simulations were carried out. The MD simulations have corroborated the experimentally determined relationships between silica tetrahedra and Al_2O_3 content as observed through Raman spectroscopy. We have also constructed a machine learning framework with a deep neural network architecture to establish a correlation between the silicate tetrahedra and the molar ratios of the slag.

Furthermore, we have devised a physical model that accurately describes the thermal conductivity of molten SiO_2-Al_2O_3-CaO slag within a temperature range of 1723−2073 K. The model can be used to describe the composition-temperature-thermal conductivity relations over entire SiO_2-Al_2O_3-CaO system.

LITERATURE

Mills *et al.*(Mills, Yuan and Jones, 2011; Mills *et al.*, 2012) noted no existing models available for estimating the thermal conductivities of slags. However, it's observed that the thermal conductivity of liquid silicate slags at their liquidus temperature increases linearly as the ratio of non-bridging oxygens to tetrahedral cations (NBO/T) decreases, *i.e.*, as Q increases. They believed that thermal conduction in slags was greater along covalent chains than across cationic bonds. This is due to slags exhibiting both covalent and ionic bonding. They also showed a link between thermal conductivity and viscosity. The temperature dependence of thermal conductivities of molten slags can be represented by the Arrhenius relation. They pointed out the measurements of thermal conductivity at temperatures on glassy and liquid slags included contributions from radiation conduction, which varied based on the measurement method. Attempts were made to estimating thermal conductivity with both Q and viscosity, but the results were not satisfactory.

Kang and Morita (Kang and Morita, 2006) determined the thermal conductivity of the SiO_2-Al_2O_3-CaO molten slags system using the non-stationary hot wire method. The measurements in temperatures ranging from the liquidus temperature to 1873 K across various compositions. They found that thermal conductivity decreased with increasing basicity (CaO/SiO_2 ratio) and showd a maximum around 15-20% Al_2O_3 content. They also noted that thermal conductivity decreased with rising temperature and discussed the effects of silicate structure depolymerization at higher temperatures.

Kang et al. (Kang, Lee and Morita, 2014) further made a comprehensive review of various methods used to measure the thermal conductivity of molten silicate slags. The authors discussed various methods for measuring thermal conductivity of molten slags, particularly focusing on non-steady-state methods. The hot-wire and laser flash methods were emphasized due to their short measurement times and suitability for high-temperature liquid phases. They also assessed the impact of slag composition and temperature on thermal conductivity, emphasizing the correlation between thermophysical properties like thermal conductivity and viscosity. The iso-thermal conductivity curves at 1673, 1773 and 1873 K, which were determined using the hot wire method, were presented.

Wang *et al*. (Wang *et al.*, 2020) studied thermal conduction mechanism of molten slag by non-stationary hot wire experimental method and a reverse non-equilibrium molecular dynamic simulation. MD simulations showed that the majority of Si in the slag forms [SiO_4] tetrahedra, with a significant portion of Al and Fe forming [AlO_4] and [FeO_4] tetrahedra. The presence of NBOs enhances the anharmonicity in the tetrahedral structure, leading to a reduction in thermal conductivity. They also defined an equivalent molar concentration of the Q_4 tetrahedron (XQ_4) and finds a positive linear relationship between thermal conductivities and XQ_4.

The relationship between microstructure of molten coal slags and thermal conductivity was studied by Wang et al. (Wang *et al.*, 2019). They found that thermal conductivity of slags was influenced by phonon vibration, which depended on the degree of polymerization in the slags. The authors presented an equation for calculating the thermal conductivity of coal slags in relation to their degree of polymerization, denoted as Q:

$$\lambda = Aexp\left(\frac{BQ}{T}\right), \qquad Q = \frac{4Q_4 + 3Q_3 + 2Q_2 + Q_1}{100}$$

This equation establishes a mathematical relationship that quantifies how changes in the slag's microstructure, particularly the degree of polymerization, affect its thermal conductivity. The relationship is derived from empirical data and analysis, reflecting the intricate interplay between the slag's chemical composition and its thermal properties.

In our previous study(Tang *et al.*, 2023), we utilized high-temperature Raman spectroscopy and Nuclear Magnetic Resonance (NMR) techniques to quantitatively analyse the microstructural characteristics of calcium aluminosilicate glasses. The results demonstrated a gradual increase in the fourfold coordinated aluminium (Al^{IV}) with the addition of Al_2O_3 to equal molar SiO_2-CaO mixtures. Additionally, significant adjustments were observed in the distribution of Qi species, indicating notable changes in the SiO_2-Al_2O_3-CaO glass microstructure. FIG 1 shows the Qi obtained from measured Raman spectra of SiO_2-Al_2O_3-CaO samples.

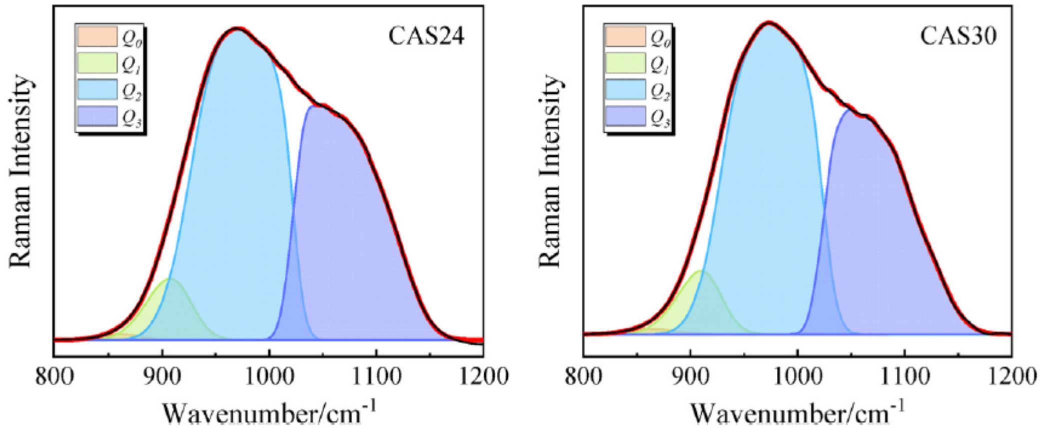


FIG 1 Qi (i =0, 1, 2, 3) distributions of Raman spectra of calcium aluminosilicate samples

A phenomenological viscosity model(Tang *et al.*, 2022) has been proposed for the description of the rheological properties covering from homogenous liquid to heterogenous partial solidified SiO_2-Al_2O_3-CaO ternary system. The model has been developed by modification of the well-known VFT formalism. As FIG 2 shown, good agreement exists between calculated and measured viscosities across a wide temperature range. This phenomenological viscosity model can be used to determination of the maximum in conductivity, usually occurs near glass transition temperature, T_g(Mills *et al.*, 2012).

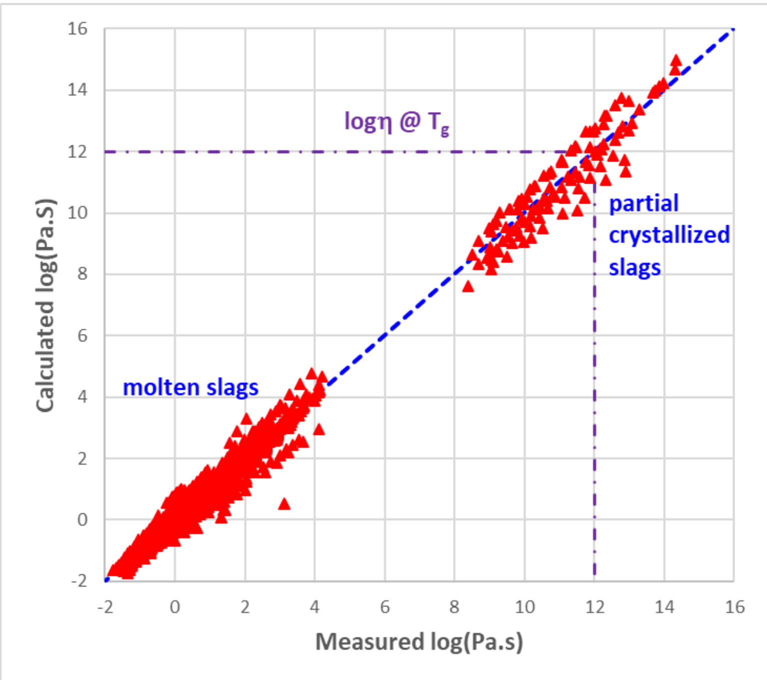


FIG 2 – Comparison of the experimental measured viscosities with calculated values by the phenomenological viscosity model

Thermal conductivity measurements at temperatures on liquid slags contain a significant and unknown contribution from radiation conduction (RC). The RC contributions are much smaller in transient hot wire (THW) measurements than for those obtained with the laser pulse (LP) method, because the emitting surface area in LP experiments is 10 more times higher than that in THW studies(Mills *et al.*, 2012). Therefore, only thermal conductivity data from THW studies were accepted in the present work. FIG 3 shows the experimental data of thermal conductivity available in the literature. The experimentally determined thermal conductivities of molten SiO_2-Al_2O_3-CaO slags exhibit considerable variability: the relative differences in measurements for identical slag compositions by different researchers often exceed 50%, and in some instances, these discrepancies can surpass 200%.

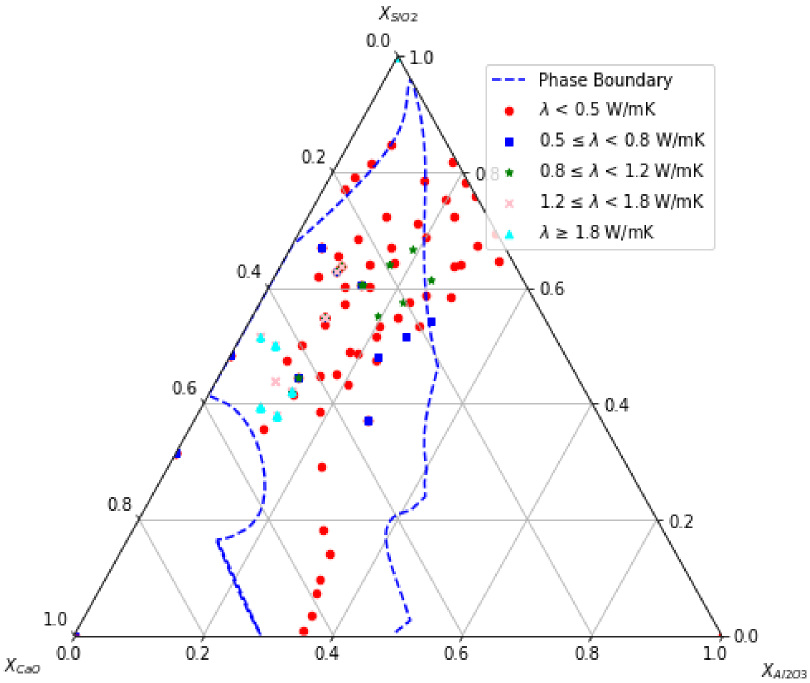
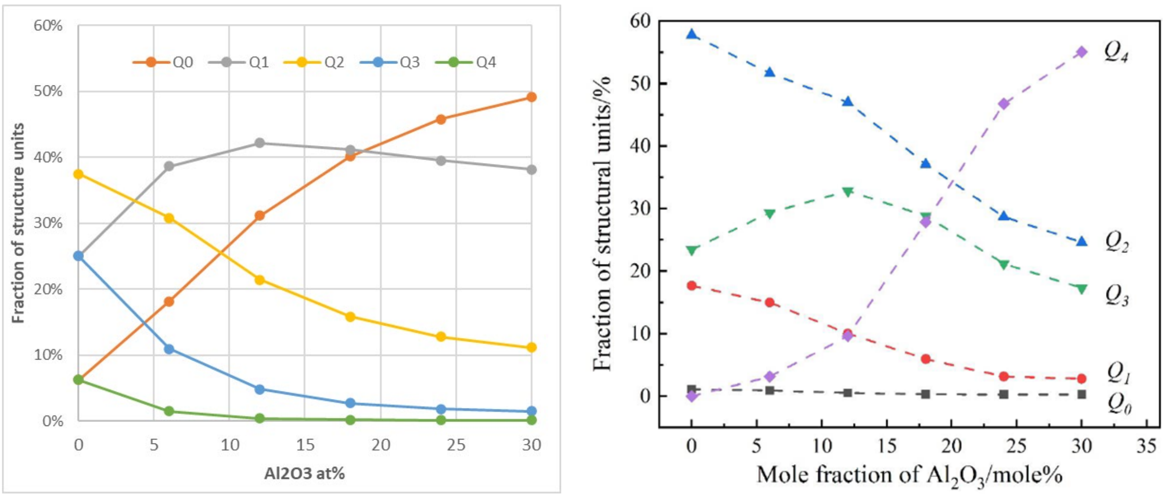


FIG 3 – Measured thermal conductivity of molten SiO_2-Al_2O_3-CaO slags reported in 1673-1973K in the literature.

METHODOLOGY

A statistical model was first developed to estimate the distribution of silicon tetrahedra in SiO_2-Al_2O_3-CaO slags across various compositions. The model was based on the contents of nearest neighbour pairs, such as Si-Si, Si-Al, Si-Ca, *etc*. as defined by the modified quasichemical model and the commercial thermochemical database, FToxid (Bale *et al.*, 2009). For more detailed insights into this model, the work of Grundy et al.(Grundy *et al.*, 2008) serves as a reference.

Unfortunately, the statistical model cannot give reasonable description of the silicon tetrahedra in the molten SiO_2-Al_2O_3-CaO oxides, as can be seen from the following figure. Although the general tendencies of Qi vary with Al_2O_3 content are rather similar, the statistical model calculations show the changing rules of Q_4 and Q_0 with the Al_2O_3 composition are exactly opposite to the measured results. The limitations of the statistical model have prompted the implementation of molecular dynamics (MD) simulations for more accurate analysis.



(a) (b)

FIG 4 Comparison of the statistic model calculated Qi (a) vs Raman determined values (b)

MD Calculation

To determine the silicon tetrahedra across the entire compositional range of the SiO_2-Al_2O_3-CaO ternary system, molecular dynamic simulations have been carried out. High-throughput MD simulations of 231 samples were performed using the LAMMPS package(Plimpton, S., 1995), covering the SiO_2-Al_2O_3-CaO ternary system in 5mol% increments. The known Jakse force field(Borboudakis *et al.*, 2017) was adopted for its accuracy. Each simulated slag composition underwent a melt-quench approach from 4000K to 2073K in the NPT ensemble. Further equilibration was conducted in the NVT ensemble followed by the NVE ensemble. Slag configuration sampling was performed in the final NVE ensemble.

Owing to space limitation, the comprehensive methodology and additional results of the molecular dynamics (MD) calculations will be detailed in a forthcoming publication.

Machine Learning

Machine learning framework has been applied to further analyse and interpret the results obtained from the molecular dynamics (MD) simulations. To model the relationship between molar fraction of species and Qi (i=0-4) at a constant temperature of 2073K, a deep neural network (DNN) with a (30,30) architecture was employed. The training of this network achieved an error rate of 0.00030 and a score of 0.9809, indicating high accuracy.

Mathematic Description of Thermal Conductivity

Since the silicon tetrahedra can now be described numerically, we are able to set up a mathematic expression for thermal conductivity of molten calcium aluminosilicate slags. As mentioned above, the temperature dependence of thermal conductivity for molten silicate melts can be expressed as Arrhenius type relation.

Recent studies revealed that the compositional dependence of thermal conductivity can be characterized by the presence of silicon tetrahedra. Effect of composition on the thermal conductivity for the present work is expressed in term of silicate tetrahedra, Qi. By examining the Qi distributions in the entire SiO_2-Al_2O_3-CaO ternary system, and using Lasso (Least Absolute Shrinkage and Selection Operator) regression(Tibshirani, 1996) for feature selection: the most important Qi for thermal conductivity. As expect, Q4 and Q0 have been selected based primary on the experimental results reported by Kang and Morita(Kang and Morita, 2006; Kang, Lee and Morita, 2014).

Integrating theoretical foundations with experimental observations, we propose a model for the thermal conductivity of the slag:

$$\lambda = (a_0 + a_1 Q_0 + a_2 Q_4) exp\left[\frac{e_0 + e_1 Q_0 + e_2 Q_4}{T}\right]$$

where a_i and e_i are the model parameters to be optimized from the experimental results.

RESULTS AND DISCUSSION

The MD simulations results can first be validated using the experimental results appeared in FIG 4(b). FIG 5 shows the similar results obtained from ML modelling results. It fits rather well with the Raman observation.

On the other hand, data from both Raman/NMR spectroscopy and molecular dynamics (MD) simulations reveal the substantial presence of fourfold-coordinated aluminium within the molten SiO_2-Al_2O_3-CaO slags, resulting in the formation of Al-tetrahedra. These structural units are expected to have a definitive impact on the thermal conductivity of the slags. However, due to constraints in manuscript length, an in-depth analysis of this effect is beyond the scope of the current discussion.

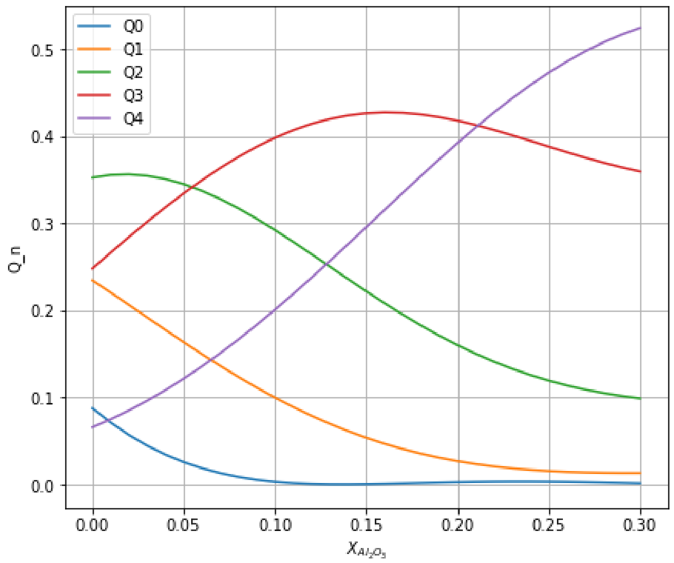


FIG 5 – ML calculated effect of Al_2O_3 contents on the distribution of Q_i species in molten calcium aluminosilicate slag

The calculated Q_0 distribution over the entire SiO_2-Al_2O_3-CaO composition range is shown in the following figure. Similarly, for the most important species, the distribution of Q_4 is shown in following FIG 7.

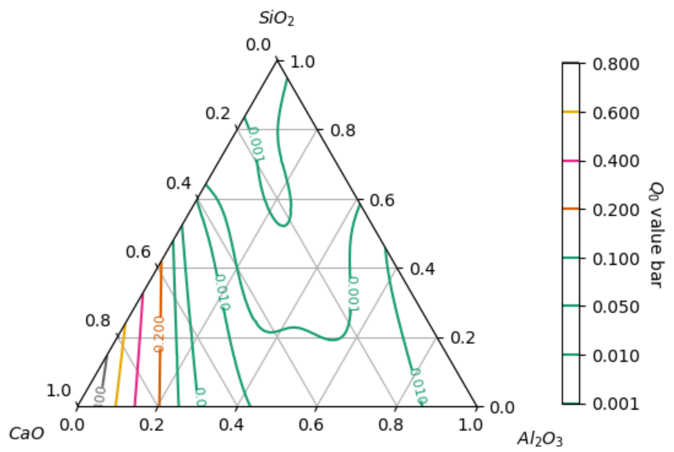


FIG 6 – Calculated iso-contours of Q_0 in the entire SiO_2-Al_2O_3-CaO system at 2073K

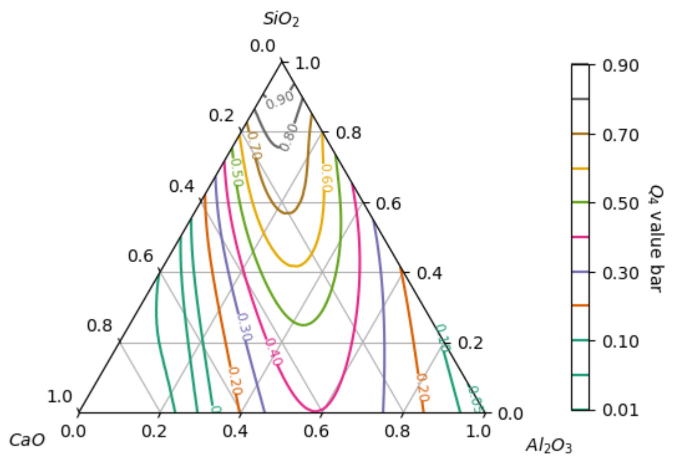


FIG 8 – Calculated iso-contours of Q4 in the entire SiO_2-Al_2O_3-CaO system at 2073K

The modelled thermal conductivity of the molten SiO_2-Al_2O_3-CaO slag at 1773K is depicted in FIG 8, alongside experimental data for comparative purposes. There is a commendable correlation between the two with a regression score of approximately 0.86 across all experimental data employed in this work.

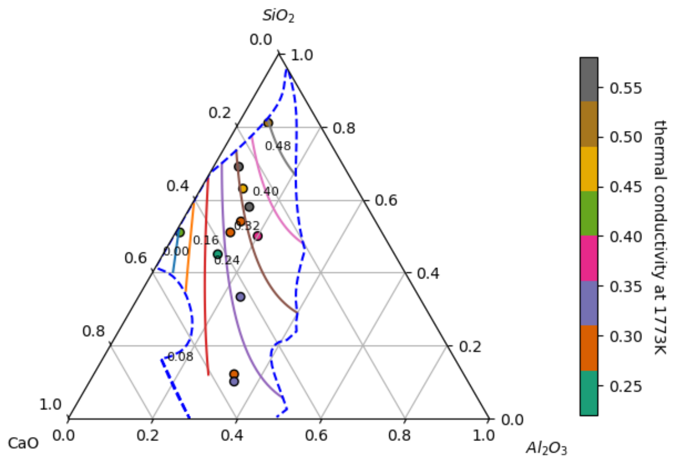


FIG 8 – Calculated iso-contours of thermal conductivity at 1773K

FIG 9 displays the calculated iso-contours of thermal conductivity at 1873K. Once more, the computational data and the trend of the contours are consistent with the results obtained from non-stationary hot wire experiments.

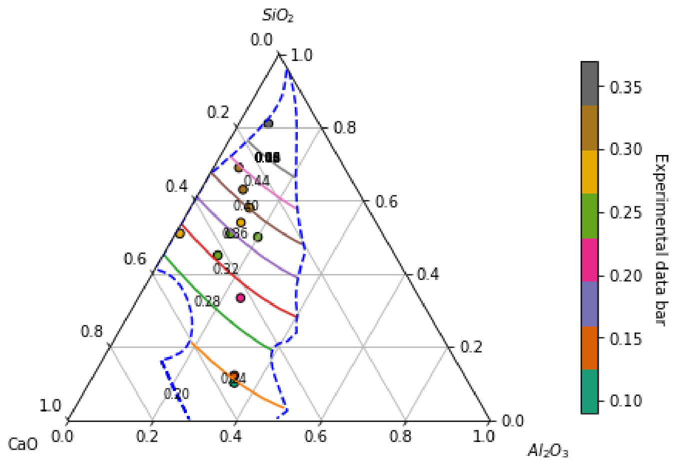


FIG 9 – Calculated iso-contours of thermal conductivity at 1873K

As mentioned earlier, thermal conductivity of liquid slag is closed related to its viscosity. Attempts have been made to include viscosity properties in the Arrhenius type relation. However, a simple implementation of the viscosity data modelled by the modified VFT model results in even worse fitting results. However, coupling viscosity and silicon tetrahedron content into deep neural networks has initially shown some promising results. Therefore, machine learning is expected to give more accurate results compared to the physical model proposed in this manuscript.

CONCLUSIONS

This study has successfully elucidated the intrinsic relationships between the microstructural properties and thermophysical behaviours of the SiO_2-Al_2O_3-CaO slag system, which holds significant relevance in metallurgy and material processes. Employing Raman and NMR spectroscopy, the essential insights into the slag structures were garnered, identifying various Qi (i=0-3) units with given composition. A deep neural network model was then employed to reproduce the statistical model calculations. Furthermore, the study successfully connected thermal conductivities with the Qi units and viscosity, utilizing empirical Arrhenius-type and neural network models, amplifying our knowledge about heat conduction phenomena in molten slags. Essentially, this work paves the way to extend these integrated methods and findings to multicomponent slags, enhancing applicability and relevance in real metallurgical and materials processing scenarios.

ACKNOWLEDGEMENTS

The current work has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 869268 (Sisal Pilot) and the Key Basic Research Projects of the Basic Strengthening Plan of the Commission of Science and Technology (2021-JCJQ-ZD-051-00-02).

REFERENCES

Bale, C.W. *et al.* (2009) 'FactSage thermochemical software and databases—recent developments', *Calphad*, 33(2), pp. 295–311.

Bouhadja, M., Jakse, N., & Pasturel, A. (2013). Structural and dynamic properties of calcium aluminosilicate melts: A molecular dynamics study. The Journal of Chemical Physics, 138(22), 224510. https://doi.org/10.1063/1.4809523

Grundy, A.N. *et al.* (2008) 'A model to calculate the viscosity of silicate melts: Part I: Viscosity of binary SiO_2 #x2013;MeO_x systems (Me = Na, K, Ca, Mg, Al)', *International Journal of Materials Research*, 99(11), pp. 1185–1194. Available at: https://doi.org/10.3139/146.101752.

Kang, Y., Lee, J. and Morita, K. (2014) 'Thermal conductivity of molten slags: a review of measurement techniques and discussion based on microstructural analysis', *ISIJ International*, 54(9), pp. 2008–2016.

Kang, Y. and Morita, K. (2006) 'Thermal Conductivity of the CaO–Al2O3–SiO2 System', *ISIJ International*, 46(3), pp. 420–426. Available at: https://doi.org/10.2355/isijinternational.46.420.

Mills, K. *et al.* (2012) 'A Review of the Factors Affecting the Thermophysical Properties of Silicate Slags', *High Temperature Materials and Processes*, 31(4–5), pp. 301–321. Available at: https://doi.org/10.1515/htmp-2012-0097.

Mills, K., Yuan, L. and Jones, R. (2011) 'Estimating the physical properties of slags', *Journal of the Southern African Institute of Mining and Metallurgy*, 111(10), pp. 649–658.

Plimpton, S. (1995) 'Fast Parallel Algorithms for Short-Range Molecular Dynamics', *Journal of Computational Physics,* 117(1), pp. 1–19.

Tang, K. *et al.* (2022) 'Rheological properties of Al2O3–CaO–SiO2 slags', *Calphad*, 77, p. 102421. Available at: https://doi.org/10.1016/j.calphad.2022.102421.

Tang, X. *et al.* (2023) 'Quantitative studies on the microstructure of ternary CaO–Al2O3–SiO2 glasses by Raman spectroscopy, 27Al MAS NMR and quantum chemistry ab initio calculation', *Ceramics International*, 49(22), pp. 34397–34408. Available at: https://doi.org/10.1016/j.ceramint.2023.07.150.

Tibshirani, R. (1996) 'Regression shrinkage and selection via the lasso', *Journal of the Royal Statistical Society Series B: Statistical Methodology*, 58(1), pp. 267–288.

Wang, Q. *et al.* (2019) 'Relationship between Microstructure and Thermal Conductivity in Coal Slags with Variable Silica and Alumina', *Energy & Fuels*, 33(7), pp. 6226–6233. Available at: https://doi.org/10.1021/acs.energyfuels.9b01090.

Wang, Q. *et al.* (2020) 'Thermal conduction mechanism based on microstructural transformations of molten slag: The role of calcium oxide', *International Journal of Heat and Mass Transfer*, 160, p. 120167. Available at: https://doi.org/10.1016/j.ijheatmasstransfer.2020.120167.