Physical properties of molten slags: Thermodynamics, transport and other properties obtained using molecular dynamics, empirical correlations, databases and neural networks

A.S. Lopis[1], M. W. Erwee[2], Q.G. Reynolds[3,4], L. Glasser[5], G.A. Venter[6], L. Malaka[3], V.S. Hilane[3] and J.H. Zietsman[7,8]

[1]Centre for High Performance Computing, South Africa
[2]SamancorCr, South Africa
[3]Mintek, South Africa
[4]Stellenbosch University, South Africa
[5]Curtin University, Western Australia
[6]University of Cape Town, South Africa
[7]Ex Mente Technologies, South Africa
[8]University of Pretoria, South Africa

The pyrometallurgy industry, representing core production capability for some of the most globally-important commodities, relies extensively on thermophysical and thermodynamic data of the materials used in its processes for the correct design and operation of furnace plants. Many of these materials such as slag (molten mixtures of predominantly metal oxides) are chemically very complex and difficult to characterise. Further challenges are associated with conducting experimental studies on materials in the molten state at temperatures in excess of 1700 K, which generally means that the availability of material property data for pyrometallurgical processes is fragmented and limited in accuracy and applicability. In this paper, alternative methods and approaches to calculation of material properties for pyrometallurgical applications are presented which leverage modern computational chemistry and materials science techniques. A case study on slags relevant in the production of ferrochromium is presented, demonstrating pros and cons of both the modern methods and more traditional empirical techniques.

INTRODUCTION

A key ingredient of stainless steel is ferrochromium (FeCr). FeCr is produced in several countries including South Africa, China, the US, Europe, Kazakhstan, and Turkey, but the largest reserves of chromite ore are in South Africa. In South Africa, which contains a significant fraction of the world's mineable FeCr resources, the chromite mining and smelting industry contributes roughly ZAR 41 billion to the country's GDP and provides over 68 000 direct jobs [1].

Mining is one of the cornerstones of the South African economy but is under ever-increasing pressure to take advantage of assets, lower costs and to become more environmentally friendly. The mining industry is also expected to maintain production volumes to sustain global demand within an environment where power supply issues remain a headache to the country at large. These pressures, however, present opportunities for fundamental research work to be deployed in an ever-more challenging environment. Research and development in understanding the smelting of chromite ore to produce ferrochromium continues around the world, with significant focus on energy efficiency, cleaner processes, alternative reductants and process stability.

The development of a deep understanding of the process of ferrochromium production has been key to the success of adapting to change. Understanding how ore, fluxes and reductants interact chemically, physically and electrically as the process temperature is increased is complex, and through systematic research on laboratory, pilot and industrial scales significant progress has been made in improving process stability and efficiency. An extensive review on ferrochrome production in South Africa is beyond the scope of this paper but a significant portion of such work continues to be disseminated through the INFACON conference series [2] and several metallurgical journals. Many of these studies and trials rely on fundamental thermochemical and thermophysical concepts to guide the work. Properties such as heat capacity, enthalpy, viscosity, electrical and thermal conductivity, density, thermal expansion, surface tension, to name a few for each of the phases involved (alloy, slag, gas, plasma), are essential in understanding and manipulating the process to extract maximum value from the ore. Without knowledge of these properties it is impossible to run a modern smelter complex or to design and commission new plants.

Properties of importance for design and operation of pyrometallurgical processes
Aside from reaction kinetics, several thermochemical and thermophysical properties are important in pyrometallurgy. In this paper, the design and operation of an electric ferrochromium process is used as an example to highlight the importance of the aforementioned properties.

Table 1 is a brief summary of properties which are required for the design and operation of pyrometallurgical processes. The relevant property is listed first, followed by technique(s) for estimation of these properties in common use. Their applicability to use in the design and operation of a furnace is then given. Note that methods for the *direct* measurement of these properties are not covered here – they are alluded to later in the paper where relevant. The reader is referred to [3], [4], and [5] for more information on such methods.

Four main techniques are mentioned in Table 1. These are:

- MD, which refers to modelling of the properties using molecular dynamics [6,7]
- RD, which refers to regression or numerical fitting of data - i.e., regression correlations for the property in question based on physical experiments
- TD, which refers to thermodynamic data - thermodynamic data models are often directly fitted onto measured experimental data to describe phases as well, but are distinguished from regression data due to the fact that the models used to describe the phases are based on fundamental theory
- SD, which refers to structural data, which relate back to TD, but based on a fundamental structural model for different phases; and
- ML, which refers to using machine learning techniques to mine either experimental data or data generated in-silico in order to estimate properties - it is here distinguished from ordinary regression models because the popularity of machine learning has increased since the first regression models were published.

The melting point (not directly addressed in this paper), heat capacity, and enthalpy of each species often top the list of 'important properties' in designing or running a pyrometallurgical furnace. These properties determine the range of operating temperature as well as the energy requirement for the process. Second to these, the viscosity and density of the molten oxide slag are often accounted for when the fluxing strategy and operating temperature is determined, to ensure that metal (often denser than slag) can detach from the slag and be fluid enough to be tapped from a furnace.

Table 1. Properties of importance in the design and operation of pyrometallurgical furnaces

Property	**Techniques**	**Application to Pyrometallurgical smelting furnaces**
Heat Capacity	MD, RD, TD, ML	Sizing and operation (energy balance), furnace refractory design, multiphase flow where energy equation is used
Enthalpy	TD, RD, MD, SD	As for heat capacity, especially for energy balance and understanding melting and phase change power supply, modelling of electrical arc
Thermal Conductivity	MD	Design and operation of furnaces, especially important for refractory lining and freeze lining management
Thermal Expansion Coefficient	MD	Design and operation of furnaces, especially important for refractory lining and buoyancy-driven flow in the melt

Many smelting processes are carried out in electrically powered furnaces. These furnaces operate at a certain electrical resistance set point to achieve maximum energy input into the process to provide heat energy for smelting. To this end, the resistivity (inverse of conductivity) of the materials in the process is often a significant consideration in the design of furnaces. Each of the properties mentioned here have been the topic of study for decades. There have been numerous successes in many of the fields of study, whilst others have lagged behind quite significantly due to the difficulties associated with performing high temperature experiments. In this paper, some of the challenges with respect to measurement are highlighted.

The importance of the correct values when modelling processes

In addition to affecting thermochemical calculations, uncertainties in thermodynamic and transport properties may also have a large impact on more complex numerical modelling of furnaces such as that applied to coupled multiphysics [8], tapping [9], particle beds [10], electromagnetics [11], and many others. The governing equations for multiphysics modelling are based on fundamental physical processes such as conservation and transport laws, and are generally well defined – but they invariably contain many parameters related to the physical properties of the materials being modelled. In the case of coupled fluid flow and heat transfer, for example, knowledge of thermodynamic properties of the fluid such as its heat capacity, density, and thermal expansion coefficient (and their dependence on temperature) is extremely important. Thermophysical transport properties such as viscosity, thermal conductivity, and electrical conductivity may also affect the system behaviour to varying degrees, depending on the problem being treated.

Without accurate and readily-available information about these properties, the value of such sophisticated modelling techniques is greatly reduced in accordance with the 'garbage in, garbage out principle'. The large uncertainties in the input parameters compound to produce very large uncertainties in the predicted results. Any improvements in physical property data for pyrometallurgical materials is therefore expected to have an immediate and tangible effect on the quality of computational multiphysics simulations, and their utility in guiding engineering design and operation decisions.

The PyroMPP consortium

Pyro Materials Physical Properties (PyroMPP) is a consortium which at present comprises the authors and institutions associated with this article. Its goal is to stimulate research and development in a broad range of methods for the estimation of thermophysical and thermochemical properties (MPPs) of the

complex and varied materials used in pyrometallurgical engineering. Current focus areas include generating targeted and general databases of MPPs, facilitating interaction between students and researchers working in the field, performing research into novel methods and workflows for obtaining MPPs, and developing software support and facilitation infrastructure. As MPPs can be obtained in a variety of ways, ranging from experimental measurement through to mathematical correlations, databases, artificial intelligence (AI) methods and computational atomistic methods, the PyroMPP consortium aims to collate and stimulate work being conducted in these disparate fields for the benefit of the pyrometallurgy industries in South Africa and worldwide.

Materials modelling using computational methods – a case study with ferrochromium slags

In this paper, six typical Fe-Cr slags are considered as examples to show the applicability of the various methods for obtaining the above-mentioned MPPs. Table 2 shows the compositions of each slag, the temperature of interest, as well as the number of atoms/ions which were used in each MD simulation box (MD info and details to follow later). Slags S1 and S2 are on the extremes of compositions for Fe-Cr slags.

Table 2. Composition of slag systems in terms of weight percentages, number of atoms in the MD simulation boxes, and main temperatures of interest

Slag	wt% Al_2O_3	wt% CaO	wt% MgO	wt% SiO_2	N_{Al}	N_{Ca}	N_{Mg}	N_{Si}	N_O	Temperatures / K
S1	38.16	6.35	24.65	30.84	372	56	304	255	1428	1900, 2000, 2100
S2	33.05	5.89	21.96	39.1	328	53	276	330	1481	1900, 2000, 2100
S3	26.1	-	38.8	35.1	248	-	466	283	1404	2000, 2040
S4	35.2	-	34.4	30.4	334	-	413	245	1404	2073, 2113
S5	25.47	14.49	17.88	42.16	250	129	222	351	1428	1779, 1819
S6	26.12	12.12	21.95	39.82	256	108	272	331	1426	1862, 1902

Sources of Thermodynamic Data

Thermodynamics provide the basic information by which to understand the behaviour of materials: principally their stability, their reactions, and the effects of temperature and pressure. Thermodynamic data has traditionally been generated by a variety of experimental methods such as calorimetry, electrochemistry, and spectroscopy, because of the great possible number of inorganic compounds. They can be complemented by quantum mechanics calculational methods (QM) which yield energies and physical properties such as elasticity [15]. Group property-sum methods are also widely available, principally for molecular systems [16]. A variety of correlation-derived methods, such as volume-based thermodynamics (VBT) [17], supplement the available data.

Further to the above mentioned data sources, access to thermochemical data and calculations in pyrometallurgy are often facilitated using the CALPHAD approach [18]. Popular software for interacting with such data include FactSage and ThermoCalc. FactSage, for example, makes it possible to determine values for heat capacity, enthalpy, and thermochemical activity for pure solid species as well as solutions such as slags and alloys. It is also possible to estimate the viscosity of slags using the FactSage software package [19]. Other popular tools for accessing thermochemical information include MTDATA [20] and HSC chemistry [21]. A detailed account of these databases is beyond the scope of this paper, but further information is generally available in the software documentation for each package.

Molecular Dynamics Methodology

Computational atomistic methods, including equilibrium molecular dynamics (MD)[6,7] and quantum mechanical (QM) approaches, are relatively novel in pyrometallurgy. A brief explanation of these methods follows. However, a detailed description of this extensive topic is beyond the scope of this paper and readers are referred to selected reference books for more information [6,7].

In MD simulations, the time evolution of a collection of atoms, ions, or molecules is calculated by applying Newton's equations of motion. To apply Newton's second law of motion, which provides velocities and consequently the evolved positions of every particle, forces can be obtained from the negative spatial gradient of the potential energy component of the total energy. The temperature at which the simulation is initiated is used to generate an appropriate distribution of the kinetic energy. The reliability of an MD simulation is therefore highly dependent on the quality of the underlying potential energy expression which, in principle, can be formulated classically or quantum mechanically; however, the simulation time lengths required to sufficiently explore phase space (the collection of all possible positions and momenta of all particles), and the need to include thousands of atoms to properly account for microscopic medium- to long-range structure as well as dynamic effects, results in a computational expense that favours the use of classical expressions for the potential energy. These classical expressions are referred to as force fields, which are typically separated into bonded and non-bonded contributions, the latter including van der Waals and electrostatic interactions. Despite including thousands of atoms that best represent the local environment around each particle, an artificial boundary surface inevitably results for a system of finite size; consequently, techniques have been developed to reinsert particles from one face of the simulation box (which is often cubic) at the opposite face, and therefore simulate the system as an infinite periodic lattice.

A resultant MD trajectory of sufficient length can then be used to calculate microscopic properties (such as structure) as the time average over many snapshots of the system, while the extension to average macroscopic thermodynamic properties is through using the principles of statistical mechanics, which lies at the heart of the relationship between microscopic characteristics and measurable macroscopic properties. The connection between the generated trajectory and statistical thermodynamics of closed systems comes from considering the collection of snapshots as representing a statistical ensemble, generated as appropriate replicas bound by the same macroscopic properties, such as the number of particles, volume and temperature (giving a canonical ensemble), or exchanging a fixed temperature for a fixed energy (the microcanonical ensemble), or replacing a fixed volume with a fixed pressure (the isobaric isothermal ensemble).

Some slag thermophysical properties of interest from MD include heat capacity [22], relative enthalpy, thermal conductivity [23], density [23] and thermal expansion coefficient [22]. Some interesting structural properties include coordination numbers, the degree of polymerisation and the radial distribution function (RDF). Transport properties of interest from MD include atomic self-diffusion coefficients, electrical conductivity [22], thermal conductivity and viscosity [22]. Interfacial and surface tensions may also be of interest in certain cases, but are not covered in the present paper.

Due to the high temperatures and harsh conditions involved in pyrometallurgy, experimental measurements can be complicated, expensive, and potentially hazardous. In addition, any experimental technique generally yields only one or two properties of interest. MD simulations, however, permit multiple MPPs to be predicted from a single set of calculations. Computational methods such as MD are relatively cheap, relatively easy, flexible and informative, allowing one to focus on features and behaviour of interest with virtually no restrictions. Once one has an established and validated MD model one can also study parts of the parameter space which are poorly understood in existing literature, correlations, databases and experiments.

The thermophysical, structural and transport MPPs mentioned in the above paragraph can all potentially be obtained from MD simulations. The present work demonstrates some of the MPPs for which there exist developed and successfully employed computational analysis methodologies - these

include heat capacity, relative enthalpy, density, volumetric thermal expansion coefficient, electrical conductivity and structural information such as coordination numbers.

Additional details of the DL_POLY [24] MD simulations performed for this paper, using the force field model of Pedone, et al. [25], are supplied in the Appendix.

RESULTS AND DISCUSSION

Heat Capacity and Enthalpy

The heat capacities and enthalpies of slags are especially important in pyrometallurgy for numerous reasons, including determining the energy requirement of a process, calculating chemical reaction equilibria, and many others.

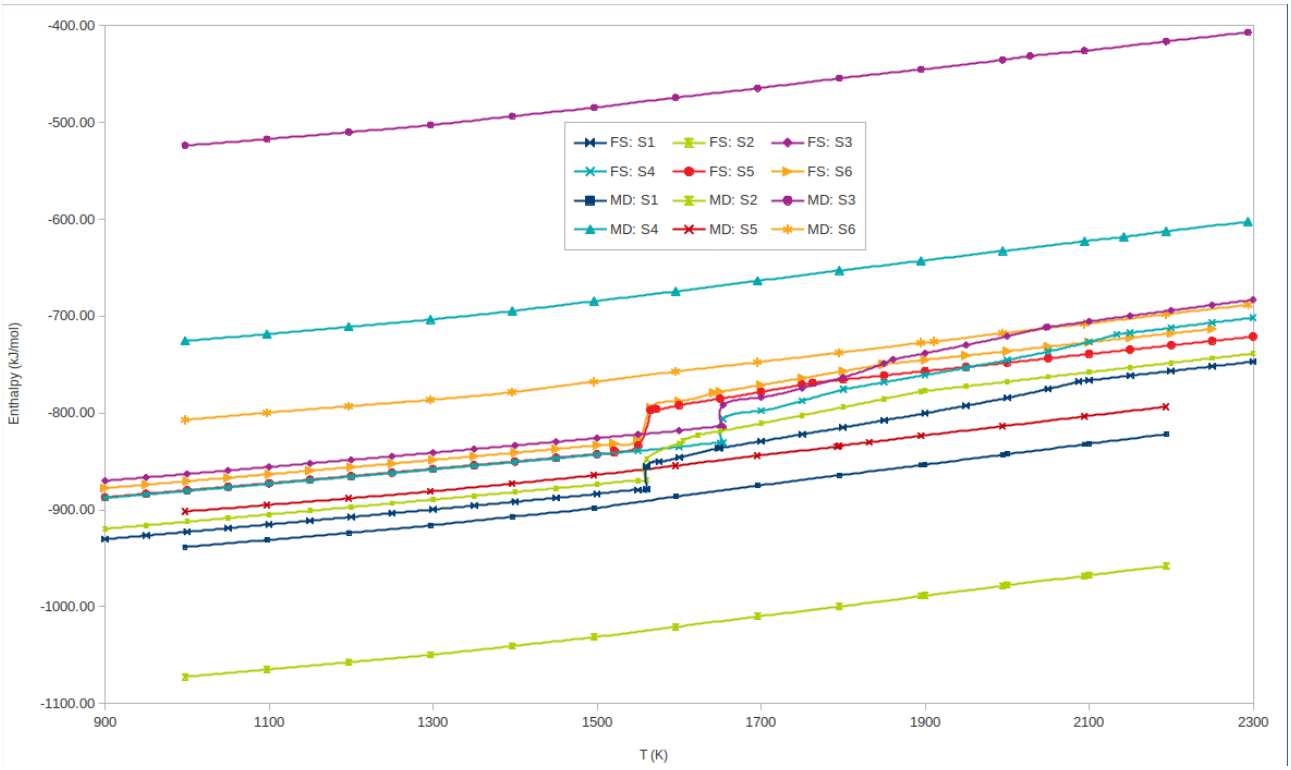

Figure 1. Comparative enthalpy-temperature relationship for the six slags of interest in the SiO_2-Al_2O_3-MgO-CaO system relevant to FeCr smelting. MD values are relative, so the curve positions have all been shifted so that the MD average value at 2200 K corresponds with the average value at 2200 K of the FactSage (FS) results.

Commercial thermochemical database tools such as FactSage are often used for such calculations. Prediction is also possible using MD methods, with some shortcomings – in particular, database models account for phase changes (heats of fusion and solution are included in the calculation), while MD currently does not. The enthalpy results from FactSage calculations and MD are compared in Figure 1. Note that since MD only generates relative values, the latter curves have been shifted by an arbitrary amount to lie in the same range as the FactSage curves. There are some differences in the enthalpy trends predicted by FactSage and MD, but they do have similarities – for example slag S3 shows the highest values, followed by S4, S6 and S5 (liquid region). S1 and S2 have the lowest values in both cases. The FactSage and MD values result from differences in chemical compositions of the slags, that is the different mineralogical phases or chemical compounds from which the slags originate. A better understanding is sought in future.

The slopes in Figure 1, which are very similar, correspond to the heat capacities at constant pressure (C_p) which are plotted in Figure 2. These C_p values are all in the same range but there are no clear trends

in the ordering of the curves. Note that the MD C_p values were determined over the visually linear range using linear regression, although a more accurate dependence of C_p on temperature may be determined if simulations are performed across smaller temperature intervals than in the current work.

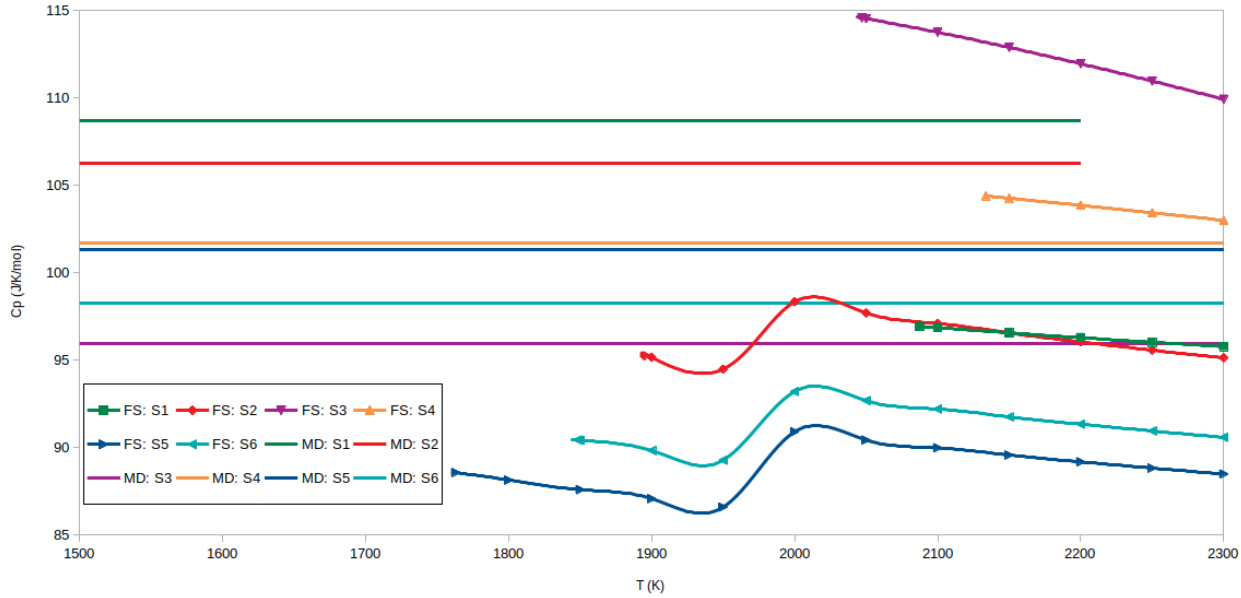

Figure 2. Comparative heat capacity C_p versus temperature relationship for the six slags of interest relevant to FeCr smelting. The FactSage (FS) C_p curves are only shown in the liquid region. The MD simulations are for the liquid phase and each C_p is a constant value calculated from the average slope of the corresponding enthalpy curve over the visually linear range.

Density and Volumetric Thermal Expansion Coefficient

In many pyrometallurgical applications, it is quite common to make a first estimate of density by means of the molar volume approach as described by Mills [5]. In this method, the molar volume of each component of a molten slag is used together with the molar fraction of said component to facilitate the calculation. In this basic approach, Mills recommends adjusting the molar volume of each component by 0.01% per 1K to compensate for changes in temperature. In this calculation it is assumed that the slag is either molten or solid when such an estimation is made, and as such the assumption on temperature dependence should be used with caution. The method is quoted to be within an accuracy of 2% for most common SiO_2-based slags.

In contrast to this basic, yet effective, calculation a more fundamental approach to improve the absolute accuracy of the calculation is demonstrated using molecular dynamics modelling [26]. By way of example, the density-temperature relationship for the six slags considered is plotted in Figure 3. Note that the slag compositions chosen (see Table 1) are for the SiO_2-Al_2O_3-MgO-CaO system, which is commonly used as a basis for slag design in ferrochromium smelting [27].

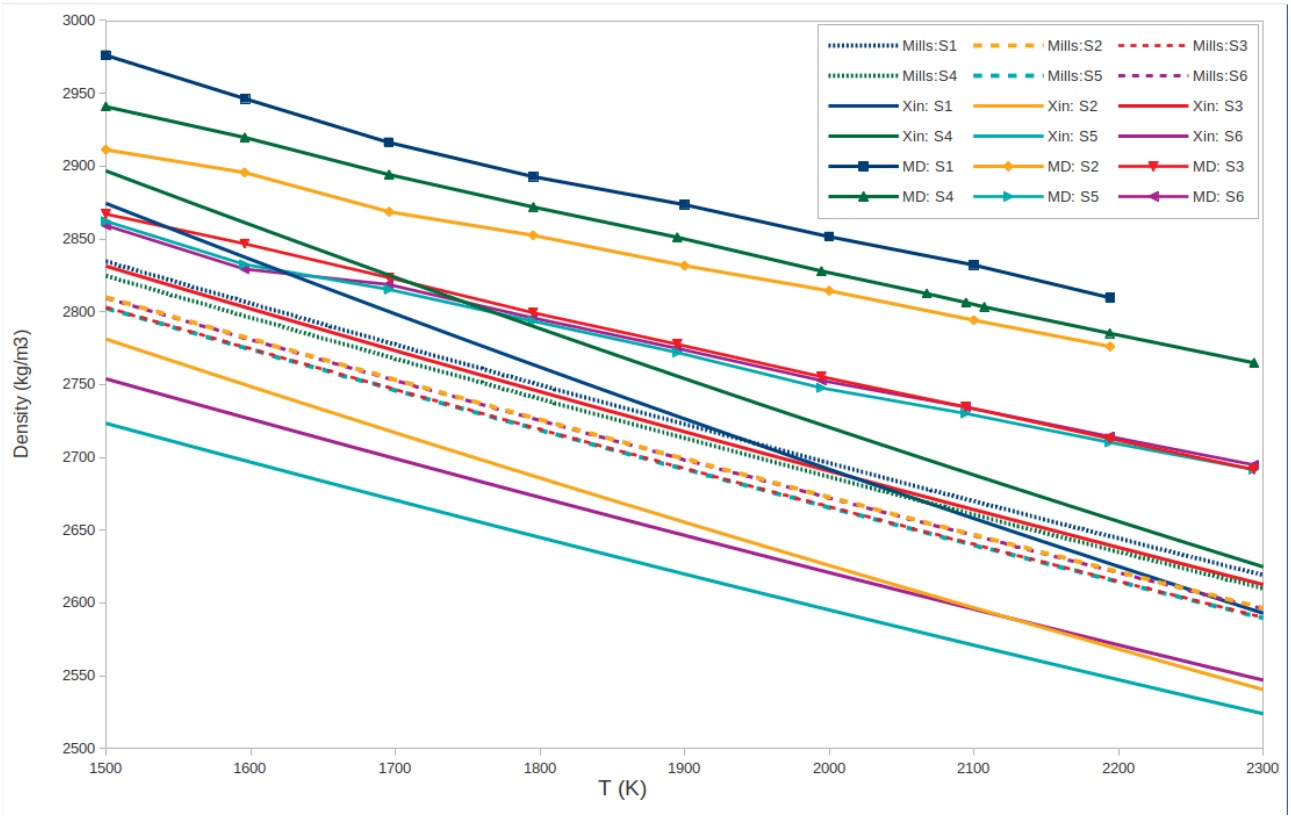

Figure 3. Comparative density-temperature relationships for the six slags of interest. The models of Mills (1987) and Xin (2017) are shown along with the MD predictions.

In Figures 3 and 4, it is important to realise that the molar volume approach suggested in Mills [5] does show significantly different values than that predicted using MD at lower temperatures. This is not surprising since MD does not necessarily distinguish between solid and liquid phases, whereas empirical correlations do so explicitly, and hence in this region the assumptions on thermal expansion differ. However, from a practical point of view, the differences in density values at higher temperatures become, in this case at least, insignificant when one considers safety factors in design and operation of furnaces - for example, knowing whether the density of a slag is 2.77 or 2.90 g/cm^3 is not as important as knowing the order of magnitude of the value relative to say the metal density of ca. 6-7 g/cm^3.

The volumetric thermal expansion coefficients in the liquid state are most useful for buoyancy-driven flow problems in the outlying regions of smelting furnaces. Given that thermal expansion has not been well studied experimentally in high-temperature slags, it is perhaps not surprising that there are significant differences between the predictions of MD and the empirical correlations. This highlights the difficulties associated with calculation of more subtle material properties using current empirical methods, whereas MD may offer a more rigorous and fundamentals-based result.

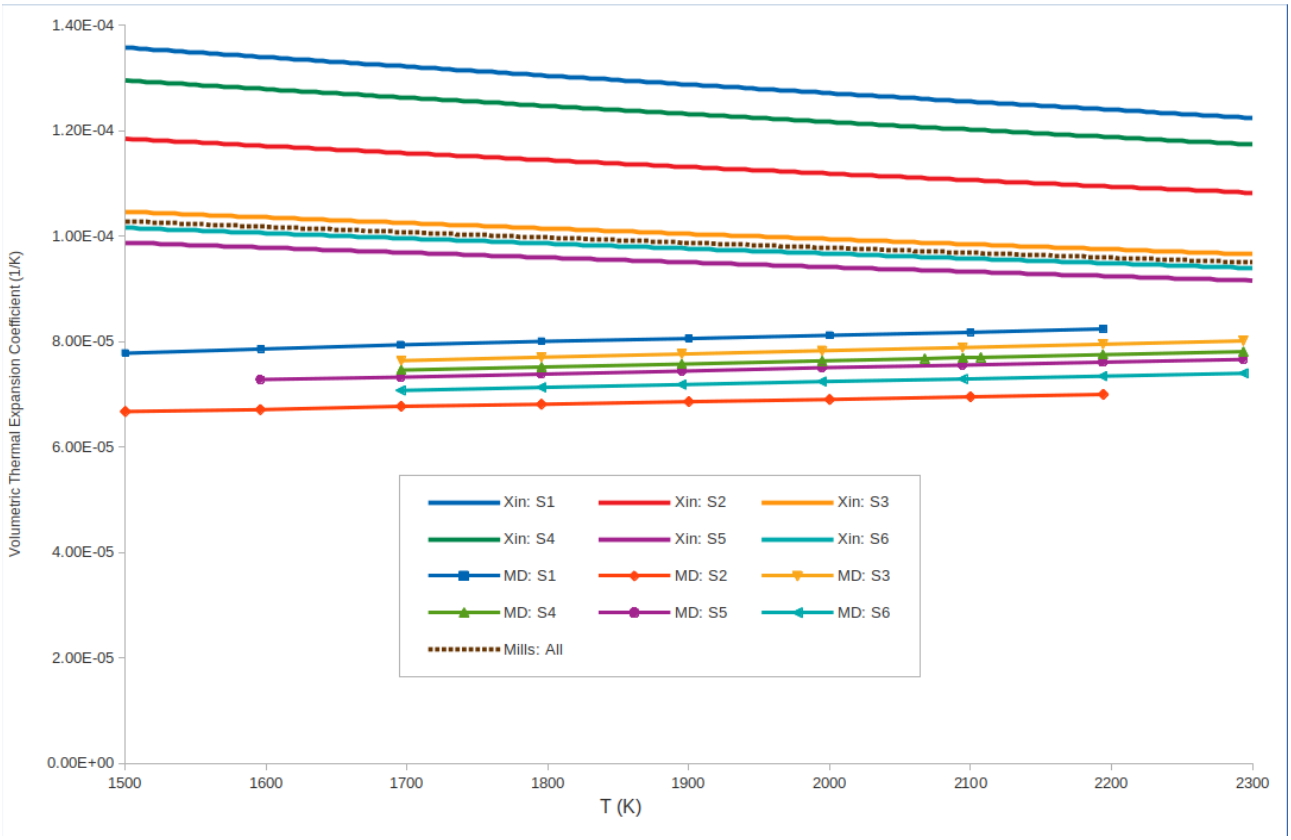

Figure 4. Comparative volumetric thermal expansion coefficient versus temperature relationship for the six slags of interest. The models of Mills (1987) and Xin (2017) are shown along with MD predictions (note that Mills' values are identical for all six slags).

Viscosity

The viscosity of slags plays an important role in furnace design and operation. Flow characteristics, slag-alloy separation, and refractory erosion are just some of the phenomena that may be affected by the viscosity of the slag. For the SiO_2-Al_2O_3-MgO-CaO system, many measurements have been done and models proposed since this system covers a wide range of commodities including ferroalloy smelting (FeCr, FeMn) as well as processes such as iron and steel making [3]. Experimental measurements have improved over time, but remain tedious and costly because of the specialised equipment and methods required to perform experiments at high temperatures.

Empirical relationships are often used to estimate the viscosity of a certain slag system, in addition to which a number of generalised models for viscosity have been proposed and are documented in the literature [28]. Artificial intelligence (AI) methods, specifically artificial neural network (ANN) methods, can be used for the data-driven prediction of viscosity; certain ANN models are stated by the authors to outperform other slag viscosity models [29,30]. Another common approach is using the viscosity calculators included in thermodynamic database tools such as FactSage [19]. In the context of FeCr smelting, FactSage predictions show reasonable agreement with measured values, specifically the values presented by Ossin in his PhD thesis [31] – this is one of the earliest datasets of its type, and one which many South African ferrochromium operations still rely on for thermophysical properties.

Standard equilibrium MD methods are unfortunately unsuitable for the determination of viscosities of many slags. Maginn, *et al.*, [32] have indicated that it is difficult to accurately predict the viscosities of systems above 0.05 Pa s (0.5 poise) using MD simulations, and they recommend more computationally-expensive non-equilibrium MD (NEMD) methods in these cases. Hence the slag viscosities shown in Figure 5 are not tractable using standard MD, except perhaps for the very lowest values. This is true for the majority of industrially-relevant slag systems, including the six slag examples considered in this

article. The exploration and development of reliable MD methods for the calculation of slag viscosity remains an open area of study at this time.

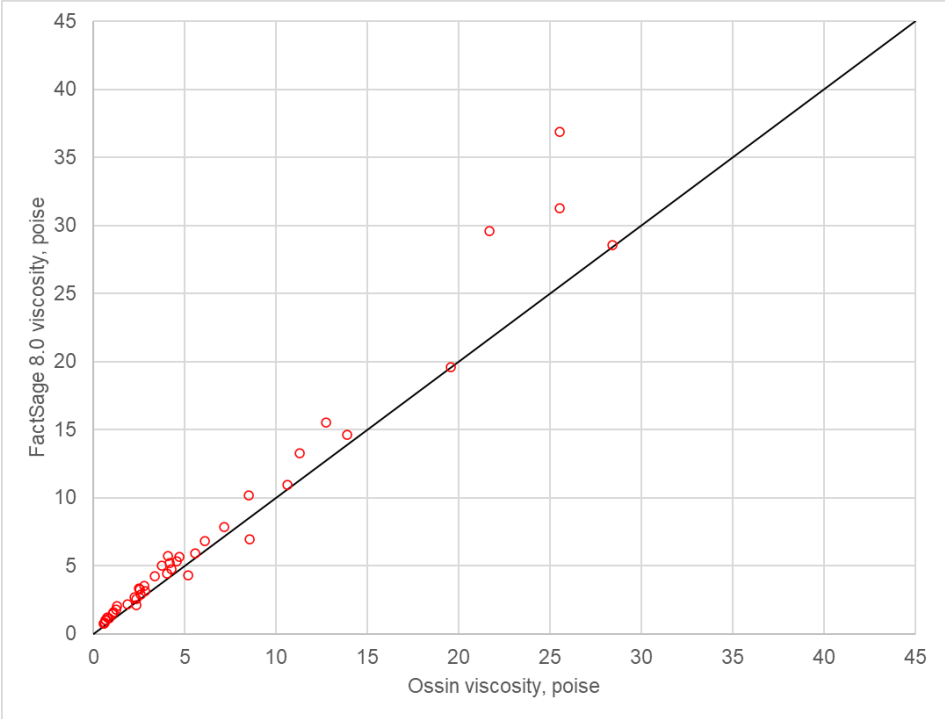

Figure 5: Correlation between the measurements by Ossin [31] and predictions from FactSage [19] for slags with compositions close to industrial FeCr operations.

Electrical Conductivity

Knowledge of slag electrical resistivity (the inverse of electrical conductivity, and referred to hereafter as 'resistivity') is important for the correct design and operation of the power supplies used by electric smelting furnaces.

In a previous publication [33], the authors used structural property information obtained from MD simulations to correctly predict resistivity values using ANN methods. Resistivity values for the six example slag systems determined by various methods are shown in Figure 6.
The empirical Jiao and Themelis correlation (J-T) [34] is commonly used for resistivity calculations, and curves for each slag are shown in Figure 6. It is, however, important to note that none of the six slag compositions are within the valid range of J-T, and hence these extrapolations are likely to include a high degree of error.

Along with measuring viscosity, Ossin [31] also measured the resistivity of some slag samples including slags S3 to S6. Based on his work, regression formulae were constructed to estimate the resistivity for a variety of slag systems of interest. Values for S1 and S2 were obtained in this way, although it should be noted that, as with the J-T correlation, the compositions of the two slags do not fall within the limits of the measured values and some extrapolation is necessarily involved.

It is not trivial to measure resistivity reliably at high temperatures, which is evident when one considers that the error in literature measurements is frequently reported to be very high. The error in measurement is usually due to difficulties with accurate positioning of the electrodes used for measurement [35] as well as polarisation effects [31]. Since the impact of these errors can be quite significant, one needs to approach interpolation of experimental data sets with care, and extrapolation beyond the limits of what was measured is not recommended.

The MD-predicted resistivities for these slags are also shown in Figure 6, and these have been obtained by post-processing the MD trajectory time series data using the more accurate explicit formulation as described in more detail in the Appendix.

When examining Figure 6, the following points are evident. The J-T resistivities are higher than the Ossin and MD values in almost every case. The Ossin and MD values differ significantly for S1, except at 2100 K. The first two Ossin values do appear as outliers from the other results having a much steeper slope; this may be a result of these values being generated by extrapolation. For S2, the Ossin and MD results agree well at 2100 K, but less well at 1900 K and 2000 K. Ossin and MD agree well for S3 and S4, while there is significant disagreement for S5 and S6 which are at relatively lower temperatures. An overall observation is that the resistivity values at the relatively lower temperatures show the biggest differences. A possible explanation for this is that more dispersed solid-phase particles occur in the slags at the lower temperatures, which is generally not accounted for in either the empirical correlations or the MD calculations [3].

It should be noted that slags with significant FeO or other transition metal oxide content (15-20 wt% or more), unlike slags S1-S6 examined here, often complicate accurate conductivity determination in experiments, correlations, MD, and other methods. This is primarily due to the occurrence of *electronic* conduction of electricity in addition to the normal ionic conduction within such slags. Since it is possible that both oxidation states of iron would occur within the slag, some Fe^{2+} cations can transfer an electron to neighbouring Fe^{3+} cations, and this process can therefore continue throughout the slag. This mechanism has been described in the literature as redox reactions [36,37], electronic conductivity [38,39,40], electron hopping [39], polaron transport [41], and polaron conductivity [40,42]. The inclusion of electronic conductivity phenomena in MD models remains an open area of research at this time, with computationally-expensive quantum mechanical methods showing the most promise.

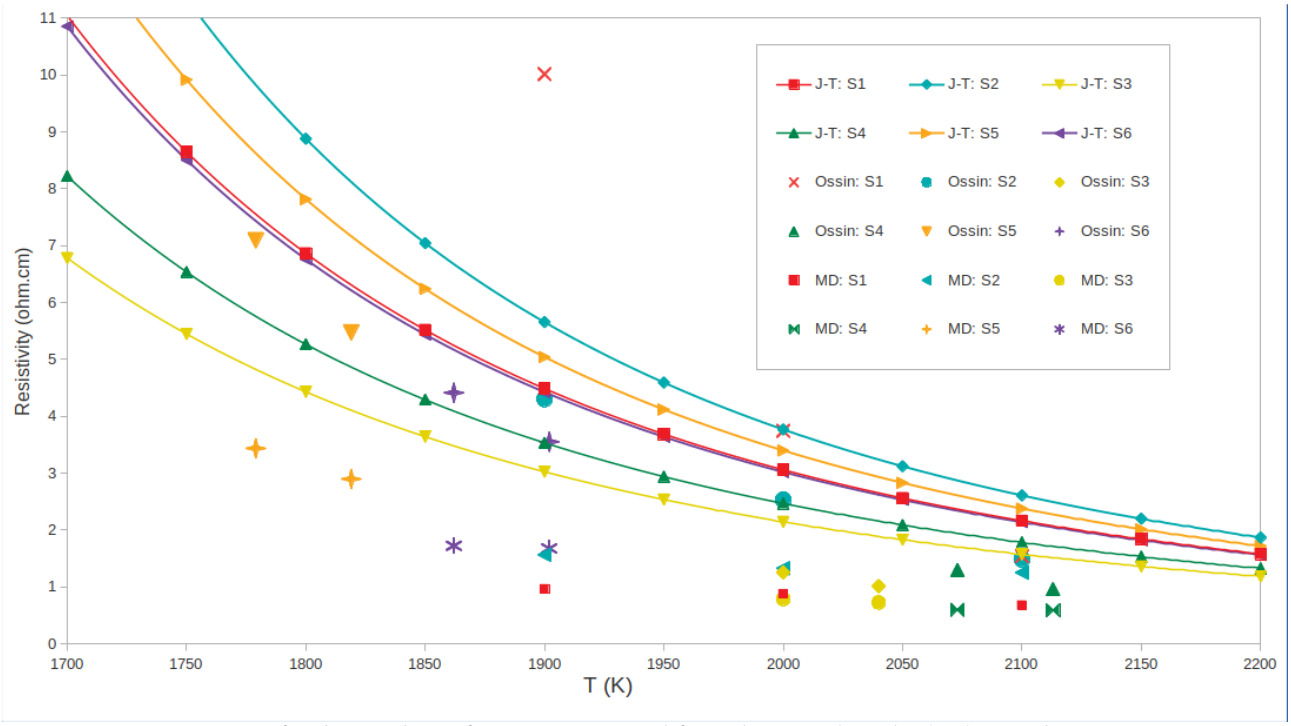

Figure 6. Resistivities for the six slags of interest generated from the Jiao-Themelis (J-T) Correlation, Ossin Experimental (S3, S4, S5 and S6), Ossin Correlation (S1 and S2), and molecular dynamics (MD) simulations.

Structural Information: Coordination Numbers

Although less obviously applicable than the primary thermophysical and thermodynamic properties discussed earlier, the structural data available from MD simulations – including coordination numbers, degree of polymerisation and radial distribution functions (RDFs) – are powerful tools to aid researchers

in understanding the fundamental underlying nature of slag systems. Structural information is also a potentially valuable source of metadata which can be included in the training of AI and other data-driven prediction models [33].

By way of example, the average coordination numbers (CN) of the oxygen anions around each cation are shown in Figure 7 for the slag systems S1-S6. The bond distance was taken as the first minimum in the respective RDFs. It was interesting to observe that there are no significant differences in CN between any of the six slags or the associated temperatures for these slags. The CN for Si-O of effectively 4, and Al-O CNs of mainly 4 and 5, are consistent with structure-forming cations. A wider range of CNs from 3 to 7 is seen for Mg-O which is expected for a structure-breaking cation, and CNs in the range 5 to 10 for Ca-O are consistent with Ca^{2+} being a structure-breaking cation with a larger effective ionic radius.

Comparing the current CN predictions with Mongalo, *et al.,* [43] who simulated at 1823K nine different SiO_2-Al_2O_3-MgO-CaO slags with a lower Al_2O_3 and MgO content and higher CaO content (of around 5, 10 and 45% by mass, respectively), reveals that the Si-O CNs are very similar, while the current CN predictions show a larger spread for Al-O, Mg-O and Ca-O. Le Cornec, *et al*., [44] also modelled a slag similar in composition to those studied by Mongalo, *et al.,* and both literature studies show similar CN results.

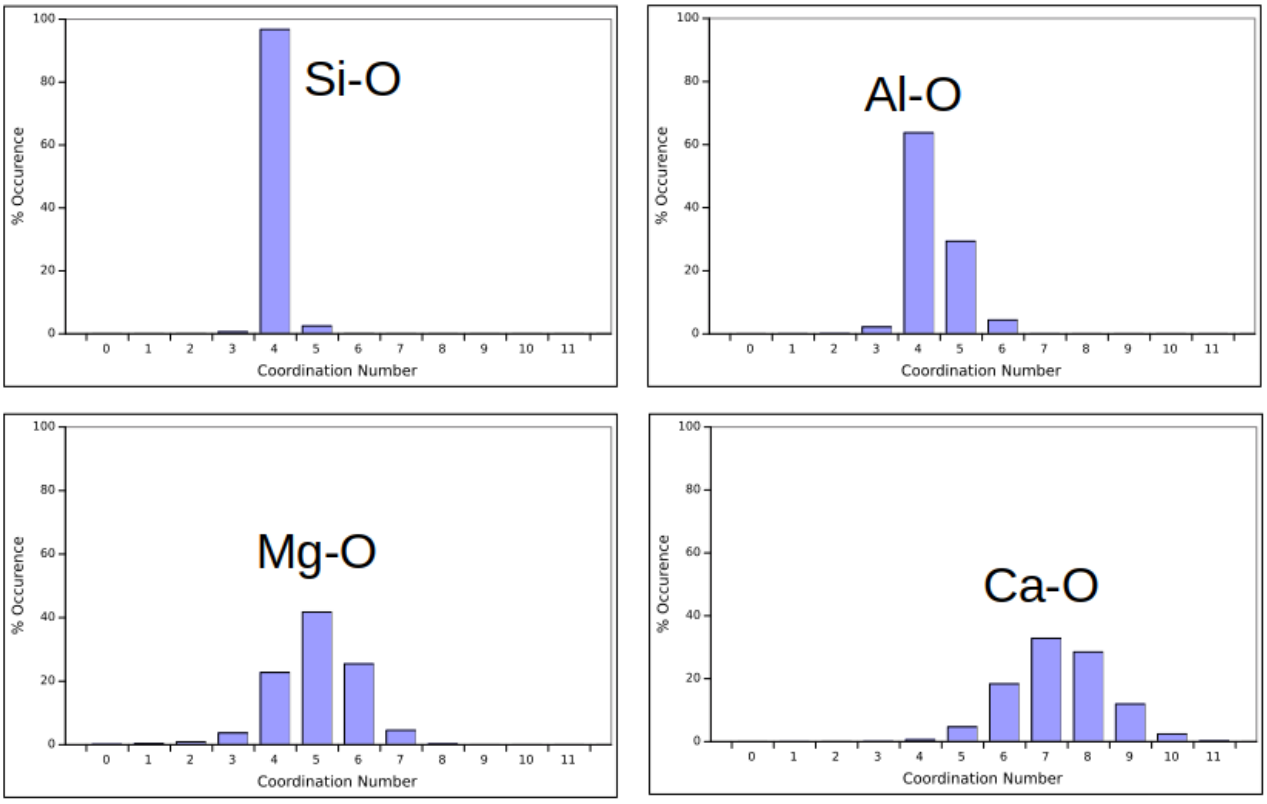

Figure 7. MD-predicted average coordination number distributions of oxygen anions around each cation. These averages apply to all six slag systems and corresponding temperatures of interest, with variations among these average distributions being minimal.

The inclusion of MD-generated structural information in semi-empirical and AI models of extrinsic material properties remain at a nascent stage of development at the current time, but it is likely that such integrated computational approaches will become more commonplace for the calculation of MPPs in the future.

CONCLUSIONS

Due to the extreme conditions involved, the pyrometallurgy industry faces a number of unique challenges when it comes to studying, engineering, and optimising its processes to fit into an ever-changing world. In particular, basic knowledge of the physical and thermochemical properties of materials involved in the pyrometallurgical production of critical industrial metals such as ferrochromium and others is often fragmented into commodity-specific pockets. Compounding this is the fact that there is limited experimental data related to these properties, and what does exist is frequently outdated and of unknown accuracy.

Methods to calculate material properties at high temperature do exist and range from simple interpolation of experimental datasets through to semi-empirical relationships based on some degree of fundamental or theoretical understanding of the material's structural behaviour. Such methods are currently the *de facto* standard in the industry, but are fraught with many of the same problems of limited accuracy and ranges of applicability associated with the underlying experimental data on which they are based.

This paper presents a brief overview and example case studies of an alternative route to the calculation of the thermophysical properties of pyrometallurgically-relevant materials. Modern computational tools such as quantum mechanics calculations, quantum mechanical and classical molecular dynamics simulations, show great promise for directly predicting the structure and dynamics of materials at the atomic scale. These methods require far less empirical information as input, and once refined and optimised, would in theory be able to predict thermodynamic and transport properties for arbitrarily complex slag and metal compositions. These computational chemistry methods, especially quantum mechanics, are however relatively computationally costly and thus time-consuming, so they are likely to be used primarily to generate extensive baseline datasets which may then be interpreted using fast, lightweight fourth industrial revolution data science tools such as neural network regression and other machine learning methods.

Although not without their challenges, such computationally-driven approaches have great potential to effect a significant step-change in the quality of the thermophysical data that pyrometallurgical engineers have to work with, especially when compared to the current state of the art. In turn, this is likely to improve furnace and process design resulting in a better, safer, and more sustainable industry.

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APPENDIX – SUPPLEMENTARY INFORMATION REGARDING MD IMPLEMENTATION

Two MD models or force fields (FF) from the literature have been used in our previous MD simulations, namely those of Guillot, *et al*. [45] and Pedone, *et al*. [25]. Initially the former was employed, but subsequently only the latter was employed for our simulations. The former research group has developed a new FF [46] of interest. Polarisable FFs [47,48,49,50] are also of future interest and QM data is often used as part of their parameterisation, especially where insufficient parameterisation data is available.

The present MD simulations were performed using the DL_POLY 2.20 code [24] along with this FF of Pedone, *et al.* [25]. The procedure for each slag simulation is as follows. A cubic box containing the appropriate number and type of ions/atoms (as indicated in Table 2) is set up using Packmol programme [51] while using an educated guess for the cell volume. Then, a fixed volume simulation is performed at 1000 K, using the canonical ensemble (constant number, volume and temperature, or

NVT) in order to equilibrate atom positions for 500 ps of simulation time. Thereafter, a series of heating calculations are performed iteratively from 1000 K in steps of 100 K up to either 2200 K or 2300 K (of 1 ns at 1000 K and 500 ps thereafter) using the isothermal-isobaric ensemble (constant number, pressure and temperature, or NPT). This ensures that the atoms within the cell and the cell volume are reasonably well equilibrated. The average cell volumes, relative enthalpy and total energy values, are monitored graphically versus temperature. From around 1400 K or 1500 K, straight line behaviour is evident indicating adequate equilibration. After confirming consistency, one employs the number, atomic masses and types of ions, to obtain essentially linear curves for density and relative enthalpy. The slopes of these curves are proportional to the volumetric thermal expansion coefficient (α) and the heat capacity at constant pressure (C_p), respectively.

Thereafter, NPT simulations of 1 ns are performed at each temperature of interest (Table 2) to obtain an equilibrated MD box of appropriate volume, with consistency checks with the density and enthalpy plots being done. NVT simulations (500 ps) are then performed at these temperatures, followed by microcanonical ensemble (constant number, volume and energy, or NVE) simulations at these temperatures, including consistency checks. Either a long NVT (1.5 ns) or NVE (at least 2 ns) simulation is used for collecting the trajectory information (the set of 'snapshots' or 'movie') with subsequent post-processing analysis to yield the required MPPs, such as transport and structural properties. The trajectory (saved in the DL_POLY HISTORY file) contains information such as the positions, velocities and forces for each atom/ion, using a specified appropriate time interval of 1 ps in our simulations.

MPPs such as density, volumetric thermal expansion coefficient (α), relative enthalpy, C_p, self-diffusion coefficients and RDFs were obtained directly from the MD output. Post-processing analyses of MD trajectory time series data was done to obtain coordination numbers and ionic electrical conductivities. The latter analysis was achieved by applying the Einstein-Helfand relation [52] to the electric flux instead of applying the alternative Green-Kubo relation [53,54,55] to this flux. These relations are both explicit ionic conductivity formulations [22] compared to the computationally cheaper, but less accurate, Nernst-Einstein (NE) approximation [56] which ignores cross terms and is directly related to the self-diffusion coefficients of the ions. The ratio of the explicit and NE calculated conductivities is referred to as the Haven ratio (H) [56] and its determination may provide useful information. Since the NE conductivity can be determined by either post processing or from the self-diffusion coefficients, it has been used as a consistency check. We are currently developing post-processing code for thermal conductivities, so this MPP has not been presented herein.

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Anton Sean Lopis

Senior Research Scientist
CHPC, NICIS, CSIR

Anton Lopis received his MSc and PhD in Computational Chemistry from the University of the Witwatersrand under Leslie Glasser and the late Fabrizio Marsicano. He then did a Postdoctoral Fellowship with Kevin Naidoo in the Chemistry Department at the University of Cape Town (UCT). Thereafter he worked as a Senior Research Officer with Jack Fletcher and Walter Boringer in the Catalysis Reseach Unit, C*Change, Chemical Engineering, UCT. Subsequently he worked as a Senior Scientist (Computational) under Kabwika Bisaka and Quinn Reynolds in the Pyrometallurgy Division of Mintek. Currently he is a Senior Research Scientist in the Centre for High Performance Computing (CHPC), National Integrated Cyber Infrastructure Systems, Council for Scientific and Industrial Research (SA). His research and publications have generally focussed on various aspects of metals such as Metal-Ligand Coordination Complexes, Solvated PGM Chlorides, and Molten Metals, Alloys, Mattes and Slags. He has continued to collaborate with Mintek on molten slag atomistic simulations after moving to the CHPC.