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Influence of SiO$_2$ Reduction on the Local Structural Order and Fluidity of Molten Coke Ash in the High Temperature Zone of a Blast Furnace: A Molecular Dynamics Simulation

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ABSTRACT

An in-depth understanding about the transformation of molten coke ash is significant to uncover the mechanism of coke reaction at high temperature inside a blast furnace. The evolution of local structural order and fluidity of molten coke ash (SiO$_2$-Al$_2$O$_3$-CaO) with the reduction of SiO$_2$ at a fixed Al$_2$O$_3$/CaO ratio was investigated by means of molecular dynamics (MD) simulation. While [SiO$_4$] tetrahedral was the main structural units forming Si-O network, due to the high levels of Al$_2$O$_3$ in coke minerals [AlO$_4$] and a small amount of [AlO$_5$] were the two key structural units forming the Al-O network. The effect of chemical composition on the bond length of Si-O, Al-O and Ca-O is very weak, while the coordination number of Al-O can be slightly influenced by the reduction of SiO$_2$ due to the unstable structure of Al-centered polyhedron compared with [SiO$_4$]. The concentration of bridging oxygen decreases, while that of tricluster oxygen increases with the reduction of SiO$_2$ from the system. Al-centered polyhedrons prefer to be connected by O triclusters, while Si-centered polyhedron favor a link by bridging oxygen. With the decrease of SiO$_2$, more [AlO$_4$] will change from edge-sharing to corner-sharing with similar units. The angular distribution of Si-O-Si exhibits an asymmetric shape with the average value around 151°, while two peaks were observed in the Al-O-Al angular distribution because of the edge-sharing (∼90°) and corner-sharing (∼122°) features in Al-centered polyhedrons. With the reduction of SiO$_2$ from the system, the diffusivity of all atoms increase considerably since the amount of strong Si-O bond decreases. Viscosity estimated from MD simulation decrease with the reduction of SiO$_2$. The good agreement between MD simulated data and experimental data indicates that MD simulation can be adopted to estimate the property change of molten coke ash at high temperature.

Key Words: coke ash; local structure; transport properties; Molecular dynamics;
1. Introduction

The depletion of sources of low-ash coals has led to an increase in the consumption of high-ash carbonaceous fuels (coal, coke, etc.) in iron making [1, 2]. In the high temperature zone of a blast furnace (BF), coke is gasified, while its mineral is converted into ash which is melted and eventually dissolved into the blast furnace slag. In our previous study on samples extracted from the tuyere zone of blast furnace, it was found that the coke ash products form a slag layer that coats the surface of coke particles [3]. The ash layer, also referred to as the mineral matter layer, was found to act as a barrier, slowing down the dissolution of coke in hot metal [4, 5] and its rate of gasification with CO$_2$ [6]. S. Gornostayev et al. [6-8] proposed that the extent of the transformation of mineral phases and their redistribution within a piece of coke at a given temperature is governed by the properties of the mineral phases themselves, i.e., by whether they reach the melting point and, after molten, by the viscosity of the molten material. The mineral particles with a lower melting temperature and lower viscosity will melt early and flow to the pore walls or surface of coke lump at the early stages of coke consumption. This will consequently cause the earlier appearance of weak spots in the coke matrix due to the formation of inhomogeneous “two-phase” system (mineral matter and a mineral-free carbon matrix) [6]. Meanwhile the less viscous melt can probably migrate for longer distances within the coke, thus providing more material for covering the pore walls and the surface of the piece of coke [6, 7]. Therefore, the flow ability or viscosity of molten coke ash is significant to the coke properties as well as its interaction with other phases.

Due to the high temperature and severe circumstance in the regions of BF where molten ash is present, extraction of intact coke samples containing ash is extremely difficult, even impossible. Further, such samples if withdrawn, would not represent the actual state of molten ash in the
process as they will undergo solidification and crystallization during the sampling process.

Because of these limitations, no reports have been published about the properties of molten coke minerals (MCM) in a BF, while an in-depth understanding of their chemistry and properties is essential to understand the mechanism of their effect on coke behavior and its interaction with other phases, and possibly using the knowledge towards optimization of coke minerals (e.g. by blending coals, cleaning, etc.) for improved fuel efficiency and reduced emissions.

This paper presents the results of an original attempt to adopt molecular dynamics (MD) simulation, for investigating the local structural order and fluidity of molten coke ashes in the high temperature zone of blast furnace. The technique has been widely employed to calculate thermodynamic, structural and transport properties of materials with high melting temperature and high vapor pressure [9]. In this study, the pair distribution function (PDF) and coordination numbers (CN) were calculated in the first place to validate the simulation technique by comparing it with experimental results obtained using high temperature neutron diffraction technique. Then, detailed information on the fractional distribution of coordination numbers for each atoms, bond-angle distributions, and concentration of bridging oxygen, non-bridging oxygen, AlO₅ units, and triclusters, as well as their changes with SiO₂ concentration were provided and analyzed. Finally, the transport properties of the melt was analyzed and the viscosity estimated with MD was compared with FactSage results and experimental results. The good agreement between all the MD results and experimental results validated that further research can be done while considering more complex coke ash system and existing conditions by the simulation technique proposed in this study.
2. Materials and methods

2.1 Sample preparation

Detailed consideration about the chosen of coke ash composition was introduced in the supporting information (session S1). Considering the reduction of SiO$_2$ in coke [10], the SiO$_2$ content was changed from 60% to 10% to replicate the effects of SiO$_2$ loss from coke minerals. The ratio of CaO/Al$_2$O$_3$ was estimated by their initial contents in the coke ash and was set to be 1/10, as shown in Table 1. In a recent study on tuyere coke [11], it was found that most of the cokes experienced temperatures above 1500 °C (1773 K) with the highest temperature exceeding 2100 °C (2373 K) when descending to the tuyere level of blast furnace. It can be confirmed that coke ashes will melt in such a high temperature. Melting points of selected melt systems were estimated with FactSage™ [12], and the results are shown in Table 1. To ensure that the selected groups of coke ash reach their melting point and keep molten state, the target temperature in this simulation was set at 1950 °C (2223 K) which was higher than the melting points of all selected coke minerals. The mean displacement and viscosity of simulated system was carefully checked to confirm that system is in molten state.

2.2 Simulation methods

The simulation method used here is based on the Born-Mayer-Higgins-Tosi-Fumi (BMHTF) interatomic potential model [13-17] which has been generally used in the research of structure of molten salt and slag [15-20] and recently adopted to investigate the structure of metallurgical melts [21-26]. The structural properties (bond length, bond angle, coordination number, etc.) obtained from simulation results with BMH model have proven to be in agreement with experimental results using X-Ray diffraction [27], Raman spectroscopy and FT-IR spectroscopy.
[24, 28], as well as neutron scattering [29, 30]. Details about this potential model and the selection of potential parameters were introduced in the supporting information (session S2).

The numbers of different atoms are decided according to the mole fractions, given that the simulation is carried out for a total number of 5000 atoms. The densities of selected melts at 1950 °C and standard atmospheric pressure were calculated based on composition and the thermodynamic properties of common oxides [31], as presented in Table 1. Assuming that all 5000 atoms are put in a cubic model box, the molar mass and density together decide the length of the simulation domain (box). Because the number of atoms in the bulk material is significantly greater than the quantities that the existing computational power can support, periodic boundary condition [9] was used and applied on all sides of the model box to create an infinite system with no boundaries so that the calculation results would be more realistic.

The MD simulation were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package, version 16 Feb 2016 [32]. All the computations were performed on the GPC supercomputer at the SciNet HPC Consortium in the Compute/Calcul Canada national computing platform [33]. Simulation procedure was introduced in detail in the supporting information (session S2).

2.3 Calculation of structural information

The pair distribution function can be used to encapsulate short-range order in melts and establish the connection between atomic structure and macro-properties that need to be understood. It describes the spherically averaged local organization around any given atom and is proportional to the probability to find an atom in the volume element $\Delta r$ at a distance $r$ from a given atom [9]. The mean coordination number is calculated by integrating the corresponding pair distribution function curve to the first valley. It provides the average total number of
neighbor atom $j$ of a central atom $i$. To investigate the structure on intermediate length scales and compare simulated data with experimental data from diffraction, the neutron structure factor was computed. Detailed introduction about the calculation of PDF, CN and structure factor was contained in the supporting information (session S3).

2.4 Calculation of transport properties

The mean square displacement (MSD) indicates the average displacement of an atom during a fixed time $L$. The self-diffusion coefficient $D$ can be calculated from Einstein’s equation $[9, 21, 34]$. Details about the MSD calculation were introduced in the supporting information (session S4).

2.5 Calculation of viscosity

To ensure the accuracy of calculated viscosity, FactSage 7.0 $[12]$ was firstly adopted to calculate the viscosity for comparison. Then viscosity was calculated with the Einstein-Stokes equation and Reverse nonequilibrium molecular dynamics (RNEMD) which are common methods in the molecular dynamics simulation process. Details about the calculation of viscosity using MD as introduced in the supporting information (session S5).

3. Results and Discussion

3.1 Variation of bond lengths and coordination number with SiO$_2$ reduction

Detailed structural characteristics, namely PDF and CN of pairs are shown in Fig. S 1 and Fig. S 2 and analyzed in detail in the supporting information (session S6). The first peaks of Si-O, Al-O, and Ca-O PDFs, which correspond to the most probable bond distances, are adopted to estimate the bond length for different pairs. The calculated bond distances of Si-O, Al-O, and Ca-O were shown in Table S 2 in the supporting information (session S6), which are in agreement with the previously published data measured by high temperature X-ray and neutron
diffraction techniques [35-37] and obtained through MD simulations [26, 38-40]. To further validate the simulation technique, the total structural factor curves of sample MCM4 (30 wt.% SiO₂), MCM5 (20 wt.% SiO₂) and MCM6 (10 wt.% SiO₂) were calculated and compared with published data obtained with high temperature neutron diffraction experimental results on similar system and at similar temperature [36], as shown in Fig. 1. The SiO₂ content in the Hennet et al’s experimental system [37] is 27 wt.% which is similar to the that of sample MCM4 (30 wt.% SiO₂). The SiO₂ content in the Jakse et al’s experimental system is 15 wt.% [36] which is similar to the SiO₂ content of sample MCM5 (20 wt.% SiO₂) and MCM6 (20 wt.% SiO₂). The test temperature for Hennent et al’s and Jakse et al’s molten systems are 1823 K and 1923 K, respectively. Even though the weight ratio of Al₂O₃/CaO is 1.82 [36] which is lower than that of the simulated samples, the curve shapes and peak positions overlap well with each other. The good agreement of peaks representing Si-O, Al-O, Ca-O and O-O between simulated results and experimental results further validated the simulation technique and potential parameters adopted.

3.2 Change of basic structural units with SiO₂ reduction

It is well recognized that [SiO₄] and [AlO₄] tetrahedrons are the fundamental structural units which are connected by sharing oxygen atoms (bridging oxygen) to form a tree-dimensional network, while Ca atoms are dispersed in the network so that each Ca provides an oxygen to break one of those network bonds. Both [SiO₄] and [AlO₄] tetrahedrons were clearly observed in the final configuration of simulated molten coke mineral samples, as shown in Fig. 2 (a) and (b) respectively. The forms of oxygen in the final configuration can be divided into bridging oxygen (BO), non-bridging oxygen (NBO) and oxygen tricluster. The bridging oxygen (BO) that connects two tetrahedron, increases the degree of polymerization, while the non-bridging oxygens (NBO, connected to one tetrahedron) has the opposite effect [21]. Depending on the
coordinated atom types, three kinds of triclusters, i.e., oxygen atoms coordinated with 3 Al atoms (O(Al, Al, Al)), 2 Al atoms and 1 Si atom (O(Al, Al, Si)), 1 Al atom and 2 Si atoms (O(Al, Si, Si)) were reported [36] and observed in the present study (shown in Fig. 2 (c) and (d)). Evolution of different types of atoms with the change of SiO$_2$ content is shown in Fig. 3. Ca atoms have the ability to create NBO by breaking Si-O and/or Al-O bonds and therefore weaken the tetrahedral network [36]. Due to the low content of CaO (< 10 wt.%) in the system, the concentration of NBO is quite low (<0.3%) and this is in agreement with the findings of Zheng et al. [26]. From Fig. 3 (a), it can be seen that the concentration of BO decreases, while that of tricluster increases with the reduction of SiO$_2$ from the system. As shown in Fig. 3 (b), the fraction of O(Al, Al, Al) increases, while fractions of O(Al, Al, Si) and O(Al, Si, Si) decreases with the reduction of SiO$_2$. It indicates that Al-centered polyhedrons prefer to be connected by O triclusters, while Si-centered polyhedron prefers to be connected by bridging oxygen.

With the reduction of SiO$_2$ (increase of Al$_2$O$_3$) from the system, number of Al-centered polyhedron will increase. As shown in Fig. 3 (c), the fraction of 4-coordinated Al decreases, while that of 5-coordinated Al increases with the increasing fraction of Al in the total system. With the decrease of 4-coordinated Al, more [AlO$_4$] units will share corners with each other, while the fraction of edge-sharing [AlO$_4$] will decrease (Fig. 3 (d)). This is also concluded from the Al-Al PDF curved in Fig. S 2 (a) B. It was also noticed that all [SiO$_4$] tetrahedrons were corner-sharing, indicating that [SiO$_4$] prefer to be connected by bridging oxygen. The presence of significant quantities of both [AlO$_5$] units and oxygen triclusters coordinated by Al reveals the complex nature of the Al-O network compared to Si-O network. Due to the low content of Ca atoms in the system and its characteristic as free cation, its coordination number does not change.
much with the reduction of SiO$_2$ and remains mainly as 5-coordinated, 6-coordinated and 7-
coordinated.

3.3 Distribution of bond angle with SiO$_2$ reduction

The distribution of bond angle with the change of SiO$_2$ content is shown in Fig. 4. The angular
distributions of O-Si-O present a quite symmetric shape in all samples averaging at about 107°
(Fig. 4 (a)), while that of O-Al-O present a shoulder on the left side of the peak position (~103°)
(Fig. 4 (b)). The configuration of different bond angles in Si-O network and Al-O network is
shown in the inserts of Fig. 4. Because of the stable [SiO$_4$] structure, only one kind of O-Si-O
angle exists in Si-O network and O-Si-O angle is very close to the ideal tetrahedral angle
(109.5°). However, at least 3 kinds of O-Al-O angles exist due to the existence of 4-coordinated
and 5-coordinated Al atoms. The distribution peak of O-Al-O angle is much wider than that of
O-Si-O due to the contribution of different types of O-Al-O angles in the Al centered
polyhedrons.

The angular distribution of Si-O-Si exhibits an asymmetric shape with the average value
around 157° (Fig. 4 (c)). With the decrease of SiO$_2$ content, the amount of Si atoms in the system
decreased, resulting in the fluctuation of averaged Si-O-Si angle values and a strong noise in the
distribution curve. Two peaks were observed in the Al-O-Al angular distribution (Fig. 4 (d))
because of the edge-sharing and corner-sharing features in Al-centered polyhedrons. As shown
in the insert of Fig. 4 (b), the different Al-centered structural units and connection types between
Al-centered polyhedrons lead to the formation of different kinds of angles, with is different from
the Si-O network (the insert of Fig. 4 (a)). The Al-O-Al in edge-sharing fashion (~90°) is smaller
than that in corner-sharing fashion (~122°). The change of chemical compositions does not
influence the angular distribution obviously.
3.4 Change of transport properties with SiO$_2$ reduction

The change of mean square displacement of Si, Al, Ca and O is are shown in Fig. 5 (a). Three different regimes with distinguishing features are observed for each atom, exhibiting typical liquid behavior, as reported in many previous works [34, 41]. In the beginning short time, atoms move on ballistic trajectories with a relationship $\text{MSD} \sim t^2$. Then, atom movement represents a “sub-diffusive” regime which shows a plateau on the MSD curve. This phenomenon in atomic diffusion was interpreted by “cage effect” which explains that O atoms are provisionally confined to cages defined by the network in the melt. The plateau time of Si is higher than that of all the other atoms since Si atom is strongly confined by the [SiO$_4$] tetrahedron. Ca atom presents a very short plateau time because it does not form network structure and can move freely in the network. With the decrease of SiO$_2$ content, the plateau time was decreased. This further confirm that the network formed by Si-O strength the connection between atoms. Following the “sub-diffusive” regime is the “diffusive regime”. In this region the atomic motion was governed by Einstein random walk and the slope of the MSD is proportional to the self-diffusion coefficient.

The self-diffusion coefficients obtained for all ions in this study and in published literature are shown in Fig. 5 (b). Tandia et al [41] obtained the data with the mass ratio of Al$_2$O$_3$/CaO being 1.82 at temperature 2400 K. Due to the higher temperature and higher CaO content, the diffusivity of atoms in Tandia et al’s research is higher than that in the present study. However, the diffusivity order of different atoms and its change with the SiO$_2$ content are in well agreement. $D_{\text{Ca}}$ is much larger than $D_{\text{Si}}$, $D_{\text{Al}}$, and $D_{\text{O}}$, indicating the diffusive nature of the non-framework cations [40]. The relationship $D_{\text{O}} > D_{\text{Si}}$ was also reported in previous research [40, 41], suggesting the restricted diffusion of the central Si within a [SiO$_4$] tetrahedron. Zheng
proposed that [SiO$_4$] and [AlO$_4$] tetrahedrals are the basic structural units in the process of diffusion and O atoms are moving cooperatively with Al and Si in the 3-dimentional network [34]. The higher diffusivity of Al than that of Si indicates the weaker bonding in Al-centered polyhedron than Si-centered tetrahedron. With the reduction of SiO$_2$ from the system, the diffusivity of Si, Al and O increases appreciably since the amount of strong Si-O bond decreases, while that of Ca fluctuated due to its small content and characteristic as free cation.

3.5 Change of fluidity with SiO$_2$ reduction

The change of viscosity calculated using FactSage, Einstein-Stokes equation, and RNEMD method was shown in Fig. 6 (a). Due to the special composition of coke ash (significantly different from common slag) and the high temperature is was located in blast furnace, no viscosity experiment has been conducted. For comparison, the experimental viscosity conducted by Solvang et al [42] for SiO$_2$-Al$_2$O$_3$-CaO system with weight ratio of Al$_2$O$_3$/CaO = 0.78~0.98 at 1849 K was also plotted. It can be seen that both simulated viscosity and experimental viscosity decrease with the decrease of SiO$_2$ (increase of Al$_2$O$_3$ and CaO at fixed mass ratio) from the system. The viscosity results obtained with Einstein-Stokes equation and RNEMD method are very close to the FactSage viscosity. The FactSage viscosity model is distinct from other viscosity models in that it directly relates the viscosity to the structure of the melt, and the structure in turn is calculated from the thermodynamic description of the melt using the Modified Quasichemical Model [12]. Since, parameters in FactSage viscosity model were optimized to fit the experimental data for pure oxides and selected binary and ternary systems, it is was proven to be accurate to estimate the viscosity of common slag system [43]. The good agreement between the MD results with experimental and FactSage results validated the simulation technique adopted in this study.
With the decrease of SiO\textsubscript{2} content (increase of Al\textsubscript{2}O\textsubscript{3} content), more [SiO\textsubscript{4}] tetrahedron is substituted by Al-centered polyhedrons. Since Al-centered polyhedrons transform into a less stable network (from [AlO\textsubscript{4}] to [AlO\textsubscript{5}], see Fig. 3 (c)), the degree of polymerization decreased with the increase of Al\textsubscript{2}O\textsubscript{3} content, resulting in the decrease of viscosity. In addition, viscosity is closely related with the oxygen types, as shown in Fig. 6 (b). The increase of viscosity is accompanied with the increase of bridging oxygen, decrease of non-bridging oxygen and oxygen triclusters. The trend of viscosity with the change of SiO\textsubscript{2} obtained in this study is in agreement with the principle proposed by J. H. Park et al. [44] based on experiment. It was found that viscosity of CaO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} system (mass ratio CaO/SiO\textsubscript{2}=1 or 1.3) increased with increasing Al\textsubscript{2}O\textsubscript{3} content up to 10 wt.%, followed by a decrease due to its nature as amphoteric oxide [44]. Since the Al\textsubscript{2}O\textsubscript{3} content of this study increased from 36.4 wt.% to 81.8 wt.%, the viscosity decreases correspondingly due to the decrease of degree of polymerization.

### 3.6 Guidance for coke reaction mechanism and further research

From the above results, it can be concluded that the viscosity of molten coke ash will decrease with the reduction of SiO\textsubscript{2} due to changes in various structural properties (bridge oxygen content decreases, oxygen tricluster content increases, diffusivity of atoms increases, etc.). Therefore, it will be easier for molten coke ash to flow out of the coke matrix through coke pores in the high temperature zone of blast furnace where SiO\textsubscript{2} was reduced to a great extent. Traditionally, the flowability of coke ash was estimated by the original coke ash composition. This needs to be corrected since most of SiO\textsubscript{2} in coke ash will be reduced in the high temperature zone of blast furnace. Chapman et al [4, 5] investigated the effect of coke ash layer (mainly Al\textsubscript{2}O\textsubscript{3} and CaO, with SiO\textsubscript{2} reduced) on the dissolution of coke carbon to liquid iron. They have confirmed that the molten coke ash will form a physical barrier between coke carbon and liquid iron and decrease
the carbon dissolution rate [4, 5]. Lower viscosity of molten coke ash will enhance carbon
dissolution from coke reaction by reducing surface blockage by ash impurities.

In addition to molten coke ash, primary and bosh slag are also likely to flow through the coke
bed and sometimes wrap the coke surface [3] (see Fig. 7). This can modify the ash composition
in the regions surrounding the coke surface. The formation of primary slag from gangue of iron
ore starts to occur in the cohesive zone of a blast furnace (about 1100 °C) and drops though the
coke column in the dripping zone of blast furnace (1400 ~ 1500 °C) [10]. However, changes of
slag composition along the height of blast furnace can be very complex due the reduction of
metal oxides (FeO and MnO) and silica during the descent of primary slag in the blast furnace. A
simplified composition of primary slag would be assumed in further research about the
modification of ash composition by primary slag. In addition, coke ash will also absorb and react
with recycling alkali vapors in the high temperature zone of blast furnace [45], which will also
modify coke ash composition. The incorporation of alkali vapors into coke ash was found to
occur at 1300 °C when coke ash was still in solid state. This incorporation resulted in volume
expansion of solid coke minerals and also influenced the matrix strength of coke [45]. However
the influence of incorporated alkalis on the fluidity of molten coke ash has not been investigated.

Further research is required to consider the properties of molten coke ash when its composition
was modified by gangue of iron ore and recycling alkalis. Even though MD simulation can
provide semi-quantitative characterization about the properties of molten coke ash, experiment
should also be adopted to test its viscosity to get the quantitative results.

4. Conclusions

The structural properties a series of ternary oxide melt system SiO$_2$-Al$_2$O$_3$-CaO with typical
coke mineral compositions were investigated by means of molecular dynamics simulation. The
following conclusions were drawn.
(1) The narrow and sharp shape of the first peak of S-O PDF curve as well as the smooth platform of $\text{CN}_{\text{Si}-\text{O}}$ curve equal to 4 at the vertical axis indicated that the [SiO$_4$] tetrahedron is very stable, while the wide and short shape of the first peak of Al-O PDF curve as well as a slanting platforms of $\text{CN}_{\text{Al}-\text{O}}$ curve demonstrated that the [AlO$_4$] tetrahedral unit are not as stable as the [SiO$_4$] tetrahedron. The influence of chemical composition on the bond length of Si-O, Al-O and Ca-O is very weak.

(2) The concentration of BO decreases, while that of tricluster increases with the reduction of SiO$_2$ from the system. In addition, the fraction of O(Al, Al, Al) increases, while fractions of O(Al, Al, Si) and O(Al, Si, Si) decreases with the reduction of SiO$_2$. It indicates that Al-centered polyhedrons prefer to be connected by O triclusters, while Si-centered polyhedron prefers to be connected by bridging oxygen. With the decrease of 4-coordinated Al, more [AlO$_4$] will become corner-sharing with other [AlO$_4$] units, while the fraction of edge-sharing [AlO$_4$] will decrease. The presence of significant quantities of both [AlO$_5$] species and oxygen triclusters coordinated by Al reveals the complex nature of the Al-O network compared to Si-O network.

(3) The angular distribution of Si-O-Si exhibits an asymmetric shape with the average value around 157°, while two peaks were observed in the Al-O-Al angular distribution because of the edge-sharing (~92°) and corner-sharing (~122°) features in Al-centered polyhedrons. The change of chemical compositions does not influence the angular distribution substantially.

(4) With the reduction of SiO$_2$ from the system, the diffusivity of Si, Al, Ca and O increases significantly since the amount of strong Si-O bond decreases and polymerization degree decreases. Both simulated viscosity decrease with the decrease of SiO$_2$, which is in good agreement with experimental results. The viscosity results obtained with Einstein-Stokes equation and RNEMD method are very close to the FactSage viscosity. The good agreement
between the MD results with experimental and FactSage results validated the simulation technique adopted in this study.

(5) Since the viscosity of molten coke ash will decrease with the reduction of SiO$_2$ due to the change of various structural properties, it will be easy for molten coke ash to flow out of coke matrix through coke pores in the high temperature zone of blast furnace where SiO$_2$ was significantly reduced. Lower viscosity of molten coke ash will benefit the coke carbon dissolution reaction since it can flow away easier. Traditional fluidity estimation method based on original coke ash composition should be improved to consider the reduction of silica.

(6) Since SiO$_2$ in coke ash will be significantly reduced in blast furnace, resulting in the change of coke ash properties, traditional evaluation of coke ash based on the original coke ash composition should be improved to considering the change of compositions in blast furnace. Future research about molten coke ash with MD should also consider the structure modification by primary slag and alkalis.

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Table Captions

Table 1 Evolution of chemical compositions of molten coke minerals, estimated melting point of solid phase using FactSage 7.0 [12]

Figure Captions

Fig. 1 Validation of total structure factors for MCM4, MCM5 and MCM6 with published neutron diffraction data [36]. The SiO2 content in the Hennet et al’s experimental system [37] is 27 wt.% which is similar to the that of sample MCM4 (30 wt.% SiO2). The SiO2 content in the Jakse et al’s experimental system is 15 wt.% [36] which is similar to the SiO2 content of sample MCM5 (20 wt.% SiO2) and MCM6 (10 wt.% SiO2). The test temperature for Hennent et al’s and Jakse et al’s molten systems are 1823 K and 1923 K, respectively. In both experiment, the mass ratio of Al2O3/CaO was kept at 1.82.

Fig. 2 Basic structural units in MCM samples: (a) Si-centered polyhedron; (b) Al-Centered polyhedron; (c) O tricluster shared by three [AlO4]5- tetrahedrons (orange), two of which sometimes have a common edge; (b) O tricluster shared by two [AlO4]5- tetrahedrons and one [SiO4]4+ tetrahedron (green) (images taken from sample MCM3, and Si, Al, Ca and O atoms are marked by balls with the color of green, orange, violet and red respectively).

Fig. 3 Evolution of different types of oxygen and aluminum atoms with the change of SiO2 content: (a) concentration of non-bridging oxygen, bridging oxygen and triclusters oxygen; (b)
fraction of different types of O triclusters in the total triclusters; (c) concentration of different aluminum atoms coordinated with different number of oxygen; (d) concentration of edge-sharing and corner-sharing tetrahedral [AlO4] in total [AlO4] tetrahedron.

**Fig. 4** Distribution of bond angle with the change of SiO2 content: (a) O-Si-O angle; (b) O-Al-O angle; (c) Si-O-Si angle; (d) Al-O-Al angle.

**Fig. 5** Transport properties of atoms in the melt: (a) mean square displacement of Si, Al, Ca and O with the change of SiO2 content; (b) Self-diffusion coefficient of Si, Al, Ca and O as a function of SiO2 content at 2223 K. The self-diffusion coefficients published by Tandia et al [41] were obtained with the weight ratio of Al2O3/CaO being 1.82 at 2400 K.

**Fig. 6** Viscosity property of molten coke ash: (a) change of viscosity calculated using FactSage, Einstein-Stock equation and RNEMD method as a function of SiO2 content. The experimental viscosity by Solvang et al [42] was obtained with weight ratio Al2O3/CaO=0.78–0.98 at 1849 K. (b) Correlation of viscosity with BO, NBO, tricluster.

**Fig. 7** Interaction of molten coke ash with primary slag and recycling alkies in high temperature zone of blast furnace.
### Tables

**Table 1** Evolution of chemical compositions of molten coke minerals, estimated melting point of solid phase using FactSage 7.0 [12], box length, atomic numbers and density of each sample at 2223 K.

<table>
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<th>Sample</th>
<th>MCM1 (60Si)</th>
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<th>MCM3 (40Si)</th>
<th>MCM4 (30Si)</th>
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