Thermodynamic assessment of the CaO-Na$_2$O-SiO$_2$ slag system

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Abstract: The primary oxide components of the bottom ash and the vitrified bottom ash slag from municipal solid waste incineration (MSWI) are CaO, Al$_2$O$_3$, SiO$_2$, Fe$_2$O$_3$, Na$_2$O and MgO. As a main subsystem, CaO-Na$_2$O-SiO$_2$ is found to be important for the phase transformation during thermal processing of the bottom ash. In the present work, thermodynamic modeling was carried out on this ternary oxide system based on literature data and authors' own the experimental results. The modified associate species model was chosen to perform the assessment and calculations, which allows a more accurate representation of the thermodynamic properties over a wide concentration range of the complex oxide system, especially for high silica composition region.

The Na$_2$O-SiO$_2$ phase diagram calculated with the newly generated database is in a good agreement with the experimental results. The pseudobinary systems CaO·SiO$_2$-Na$_2$O·SiO$_2$ and Na$_2$O·2SiO$_2$-Na$_2$O·2CaO·3SiO$_2$ were evaluated. The phase diagram in the more than 50 wt% silica region of the ternary system is predicted reasonably well in comparison with experimental data. The phase relations in low SiO$_2$-containing area and phase Na$_2$O·3CaO·6SiO$_2$ need to be further refined. A group of model parameters was obtained which will be used to evaluate quaternary and more complex oxide systems in the future.

Key words: Bottom ash vitrification, Phase relations, Associate slag model, Thermodynamic assessment, Optimization.

1. Introduction

The complex bottom ash slag formed during municipal solid waste (MSW) incineration can be transformed into glassy slag by vitrification. According to the previous publication [1], SiO$_2$, CaO, Al$_2$O$_3$, Fe$_2$O$_3$, Na$_2$O and MgO account for more than 90% of the bottom ash by weight for typical Dutch waste incinerators. The ternary system Na$_2$O-CaO-SiO$_2$ was found to be important for the phase relations during the thermal processing of the bottom ash. In addition, this ternary system has also attracted much research attention due to its importance to the glass industry [2, 3, 4, 5].

The phase relations in the Na$_2$O-CaO-SiO$_2$ system at less than 50 wt% SiO$_2$ concentrations have been experimentally investigated at temperatures between 1200 °C to 1400 °C in the previous study [6]. However, experimental measurements on the complex slag system for the whole range of composition and temperature are difficult. Compared to experimental methods, thermodynamic calculation can predict the phase relations for a broader region within a shorter time and at less expense, if the calculation results are properly validated. Phase relations for the whole interesting region of the system CaO-Na$_2$O-SiO$_2$ can be calculated with thermodynamic modeling. Moreover,

the thermodynamic database built for the system can be extrapolated to quaternary or multi-oxide system. Investigations have shown that the available databases for this system are not sufficient to model the thermodynamic properties. The selection of a proper slag model for establishing the database of the oxide system is a prerequisite. Different models [7, 8, 9, 10] have been suggested for modeling chemical thermodynamic behavior and phase relations of complex oxide systems. In the present work, Calphad modeling was carried out for CaO-Na_2O-SiO_2 ternary system, effort was given to optimize the model parameters, and thus to compute and predict Na_2O containing multi-components phase diagrams.

2.   Thermodynamic slag models

In recent years, several thermodynamic databases for multi-component oxide have been developed with the Calphad modeling technique. The thermodynamic models are chosen for the phases description of their thermodynamic properties and crystal structure. The model parameters are optimized to reproduce all reliable experimental data within experimental error limits. Apparently, a thermodynamic model that adequately describes the enthalpy, entropy and Gibbs energy of the slag as functions of temperature and composition is essential. To be useful for this purpose, a model must be sufficiently realistic to have a good predictive ability, but not be so complex and mathematically intractable.

Molten oxide slags are usually ionic liquids with complex network structure and have specific short-range periodicity which is a function of composition. The liquid phase of the complex oxide system can be described with different approaches such as: the modified quasichemical model [7], the ionic two sublattice model [8], the cell model [9] and the associate species model [10]. The modified quasichemical model has been ued for the FACT slag database of FactSage [11]. This model involves determining the interactions or bonding between second-nearest-neighbor metals. The energy change in establishing those bonds or interactions is represented by a mathematical expansion in composition. For multi-component systems, these compositions typically must be determined by fitting the phase equilibria and other properties for each constituent binary system as well as some ternary and quaternary systems. The result has been a multiplication of terms that makes the systems quite complex.

The Cell Model [9] treats the melt as a mixture of cells such as (A–O–B), where A and B are cations in the melt. In the Cell Model, the Gibbs energy of a ternary solution is calculated from the binary parameters using the Toop-like interpolation technique with the most acidic component as an asymmetric component, which is similar to the modified quasichemical model. Although the configuration entropy term of the Cell Model is somewhat different from that of the modified quasichemical model, the basic concepts of both models are identical. The two sublattice model was developed by Hillert et al. [8] and used as a standard model for the oxide melt database in Thermo-Calc [12]. For the alkali-silicate systems no data assessments using the cell model or the two sublattice solution are known in the literature [13].

The associate species model was first developed by Hastie and Bonnell [10] for complex oxide solutions in order to obtain vapour pressure data. The basis of this approach is that the strong chemical interactions in complex oxide solutions can be represented by the formation of intermediate associate species from pure oxide and end-member components. The associate species and the end-member component are assumed to form an ideal solution. However, the relatively weak repulsive interactions which lead to miscibility gaps in many silicate systems cannot be accounted for

by this method. The modified associate species model [14] avoids the use of interaction parameters with the exception of immiscible phase regions, which require positive interaction energies. The additional associate species are used instead of any interaction parameters and non-ideal interactions between the end-member constituents and the associate species are taken into account in this model. It can accurately represent the thermodynamic behavior of very complex chemical systems over wide temperature and composition ranges. It can also logically estimate the unknown thermodynamic values with accuracy greater than required for predicting useful engineering limits and be easy for non-specialists in thermochemistry to understand and use.

According to the modified associate species model [14], the molar Gibbs energy of the solution is expressed by an equation in the form of the sum of its reference part, its ideal and its excess part as:

$$G_m = \sum x_i G_i^0 + RT \sum x_i \ln x_i + \sum_{i<j} \sum x_i x_j \sum_v L_{ij}^{(v)} (x_i - x_j)^v \qquad (1)$$

Where x_i is the mole fraction of phase constituent i (including the associated species), G_i^0 is the molar Gibbs energy of the pure phase constituent i and $L_{ij}^{(v)}$ is an interaction coefficient between components i and j, according to the Redlich-Kister polynomial. $L_{ij}^{(v)}$ is a temperature dependent term according to:

$$L_{ij}^{(v)} = A_{ij}^{(v)} + B_{ij}^{(v)} T + C_{ij}^{(v)} T \ln T + D_{ij}^{(v)} T^2 \qquad (2)$$

To provide equal weighting of each associate species with regard to its ideal mixing entropic contribution, each species contains a total of two non-oxygen atoms in its formula [14]. Ternary and high order interaction terms can easily be added to Equation if needed.

In the present work the modified associate species model is employed since it allows an adequate representation of the thermodynamic properties in more extended concentration ranges. In this model, interaction parameters were used whenever they are needed to get a better description of any part of the system.

3. Data assessment

The Gibbs energies of liquid phases in the binary systems Na_2O-SiO_2, CaO-SiO_2 and CaO-Na_2O-SiO_2 were re-assessed using the modified associate species model. This model uses intermediate liquid chemical species with their corresponding thermodynamic data to represent the negative free-energy terms caused by non-ideal mixing of the end-member components in the oxide systems. Both data for the Gibbs energies of the pure associates and data for the interaction terms in the Redlich-Kister equation are assessed. The new solution data for the modified associate species model were optimized in the assessment procedure. In the optimization the thermodynamic data for the pure solid and liquid compounds were kept constant. The following parameters were chosen to be adjustable: standard formation enthalpies ΔH_{298}^0 and entropies S_{298}^0 of the considered additional liquid species and the interaction parameters between solution constituents $L_{ij}^{(v)}$ in equation (2).

The optimization procedure was conducted with the optimization module in the FactSage computer program [13]. The primary experimental data used are those of the phase diagram. The data were analyzed with respect to their relevance and consistency. In the optimization procedure, the standard formation enthalpies and entropies of liquid

associate species were determined firstly. During this step, the interaction parameters were set to zero. Then the interaction parameters were added where necessary. After execution of the optimization, the new thermodynamic database including properties of pure solid, liquid, solution species and the set of interaction parameters were obtained.

In the present work, the Fact Pure Substance database was used as basis because it contains the most complete data set for compounds, pure solid, liquid and gaseous phases regarding complex oxide system. Formation enthalpy and entropy data of the pure solid compounds Na_2O, SiO_2, CaO and calcium silicates are from the FACT database [15]. The thermodynamic data of sodium silicates are from Spear's database [16] which was built for describing thermodynamic properties of silica refractory corrosion in glass-melting furnaces. All the thermodynamic data were firstly assessed to describe the phase equilibria relations of the sub-binary systems $Na_2O\text{-}SiO_2$ and $CaO\text{-}SiO_2$. Table 1 provides a complete list of the thermodynamic properties of solid, liquid and associate species obtained from literature and optimized in the current assessment.

Table 1. Thermodynamic data in the $CaO\text{-}Na_2O\text{-}SiO_2$ system: formation enthalpy and entropy data of the pure solid and liquid compounds and liquid associate species

Species	ΔH^0_{298} (J/mol)	S^0_{298} (J/mol K)	T(K)	$C_p=a+b \cdot T+c \cdot T^2+d \cdot T^{-2}$ (J/mol K)			
				a	$b \cdot 10^3$	$c \cdot 10^6$	$d \cdot 10^{-5}$
Solid							
Na_2O[a]	-417981.6	75.040	298-1405	82.562	12.350	0	0
$SiO_2(cris)$[a]	-907257.0	47.629	298-2980	52.170	24.004	-4.0680	-13.311
$SiO_2(trid)$[a]	-910700.0	41.460	298-2960	47.451	24.006	-4.0690	-13.307
$SiO_2(quar)$[a]	-910290.0	41.943	298-2960	47.451	24.006	-4.0690	-13.307
Na_2SiO_3[c]	-1558601.2	113.85	298-1363	234.77	0	0	0
Na_4SiO_4[c]	-2101297.4	195.81	298-1393	162.59	74.224	0	0
$Na_2Si_2O_5$[c]	-2470340.1	164.05	298-1148	250.69	0	0	156.51
	-2470340.1	164.05	1148-1250	261.21	0	0	0
$Na_6Si_2O_7$[c]	-3596079.5	360.83	298-1397	461.01	0	0	-203.69
$Na_6Si_8O_{19}$[c]	-9167917.2	652.86	298-1082	987.69	0	0	-355.41
CaO[a]	-566563.2	59.042	298-1830	52.863	0.31000	1.1350	-9.7880
	-566563.2	59.042	1883-2880	212.69	-109.83	22.730	-1034.6
$CaSiO_3(S1)$[a]	-1634049.1	81.993	298-3000	112.35	16.053	0	-28.750
$CaSiO_3(S2)$[a]	-1625868.2	88.342	298-6000	107.52	18.976	0	-23.290
$Ca_2SiO_4(S1)$[b]	-2320823.6	120.57	298-6000	131.48	52.467	0	-17.980
$Ca_2SiO_4(S2)$[b]	-2296705.6	136.65	298-6000	165.48	22.950	0	-44.525
Ca_3SiO_5[b]	-2935928.2	168.69	298-6000	211.45	36.130	0	-44.926
$Ca_3Si_2O_7$[b]	-3951761.0	210.89	298-6000	251.38	58.981	0	-48.261
Na_2CaSiO_4[d]	-2240434.6	156.77	298-1668	284.69	-65.302	22.720	-150.78
$Na_4CaSi_3O_9$[b]	-4772500.0	321.21	298-1996	474.51	9.8200	0	-125.67
$Na_2CaSi_5O_{12}$[b]	-5947700.0	337.06	298-1996	513.17	13.580	0	-203.79
$Na_2Ca_2Si_2O_7$[d]	-3940003.0	238.49	298-3172	363.29	-7.2830	5.5570	-107.81
$Na_2Ca_2Si_3O_9$[b]	-4885012.0	279.81	298-1996	420.33	0.014000	0	-134.16
$Na_2Ca_3Si_6O_{16}$[b]	-8357600.0	451.04	298-1996	685.64	23.820	0	-259.83
Liquid							
Na_2O[a]	-356602.3	120.29	298-1023	27.219	15.349	-96.575	4.1820
Si_2O_4[a]	-1805280.0	95.258	298-2980	103.34	48.007	-8.1360	-26.622
Na_4SiO_4[c]	-2010756.2	262.27	298-1358	325.18	148.44	0	0
Na_2SiO_3[c]	-1514367.3	139.90	298-1363	469.54	0	0	0
$Na_2Si_2O_5$[c]	-2444942.0	183.20	298-951	250.69	0	0	-156.51
Ca_2O_2[a]	-1133126.4	118.08	298-1830	105.72	0.62200	2.2700	-19.576
$CaSiO_3$[b]	-1597518.2	101.60	298-1830	105.03	24.315	-2.9330	-23.099
Ca_2SiO_4[b]	-2230212.4	167.55	298-1830	157.89	24.626	-1.9780	-32.888

[a] Data of these species were taken from the FACT database [15]. [b] Data of theses species were optimized based on the FACT data [15]. [c] Data of these species were from Allendorf and Spear database [16]. [d] Data of these species were estimated with the molecular ratios of the individual pure oxide and optimized subsequently .

The CaO-SiO$_2$ system is complex to treat for liquid-liquid immiscibility using the modified associate species approach. Such immiscibility requires the solution to be treated as non-ideal, having positive interaction energies. The liquid for the CaO-SiO$_2$ system contains the end-member species CaO$_{(l)}$ and SiO$_{2(l)}$ plus the associate species CaSiO$_{3(l)}$ and Ca$_2$SiO$_{4(l)}$. For the two incongruently melting component Ca$_3$SiO$_5$ and Ca$_3$Si$_2$O$_7$, the liquid phase data are not essential to describe the phase relations. The phase equilibria in these two region can be represented by the interaction parameters between CaO$_{(l)}$ and Ca$_2$SiO$_{4(l)}$, SiO$_{2(l)}$ and Ca$_2$SiO$_{4(l)}$. The liquid-liquid immiscibility region requires the inclusion of non-ideal interaction terms which were determined between CaSiO$_{3(l)}$ and SiO$_{2(l)}$.

In the binary system Na$_2$O-SiO$_2$, the liquid solution includes two pure liquid oxides Na$_2$O$_{(l)}$, SiO$_{2(l)}$ and three associate species Na$_4$SiO$_{4(l)}$, Na$_2$SiO$_{3(l)}$ and Na$_2$Si$_2$O$_{5(l)}$ which are given in Table 1. The phase relations of the system Na$_2$O-SiO$_2$ has been assessed by Yazhenskikh [13]. In the present assessment the thermodynamic data of the binary components were taken from Allendorf and Spear [16]. Formation enthalpy and entropy of the binary solid and liquid species were re-assessed by adopting the experimental results in literature [17, 18, 19]. The interaction parameters of liquid species in Na$_2$O-SiO$_2$ were optimized to achieve the best overall agreement with the most accurate experimental information reported for each phase and the phase diagram. The parameters between Na$_2$SiO$_3$ and Na$_2$Si$_2$O$_5$, SiO$_2$ and Na$_2$Si$_2$O$_5$ were refined. The parameters between SiO$_2$ and Na$_2$SiO$_3$, which were not presented in Yazhenskikh's [13] study were also given in this study. The resulting interaction parameters of liquid phases in the CaO-Na$_2$O-SiO$_2$ system are given in Table 2.

Table 2. Interaction parameters of the modified associate model for liquid species in the CaO-Na$_2$O-SiO$_2$ system

| Species 1	Species 2	A_{12}^0	B_{12}^0	A_{12}^1	B_{12}^1
Na$_2$O[a]	Na$_4$SiO$_4$[a]	6643.0	0	0	0
Na$_4$SiO$_4$[a]	Na$_2$SiO$_3$[a]	48.6	0	-66.4	0
Na$_2$SiO$_3$[a]	Na$_2$Si$_2$O$_5$[a]	975. 9	3.3	-84.6	4.9
SiO$_2$[a]	Na$_2$Si$_2$O$_5$[a]	7061.6	9.6	435.6	-8.9
SiO$_2$[b]	Na$_2$SiO$_3$[b]	14905.9	-28.3	308.9	-24.4
SiO$_2$[c]	CaSiO$_3$[c]	154399.2	-72.0	-69700.0	17.0
SiO$_2$[c]	Ca$_2$SiO$_4$[c]	143000.0	-70.0	-10000.0	-10.0
CaO[c]	Ca$_2$SiO$_4$[c]	-4200.0	0	0	0
CaSiO$_3$[b]	Ca$_2$SiO$_4$[b]	31313.2	-13.9	-26000.0	18.4

[a] Parameters between theses species were from Yazhenskikh [13]. [b] Parameters between these species were optimized in this study. [c] Parameters between these species were taken from Besmann and Spear [14].

For the CaO-Na$_2$O-SiO$_2$ system, the thermodynamic data of the ternary solid species from FACT database were used as original data. The data that are not included in FACT database were estimated with the relative molecular ratio from pure solid compound CaO, Na$_2$O and SiO$_2$ as basis for optimization. In principle, all these basic thermodynamic data were optimized according to the experimental results [6, 20, 21]. Segnit [20] and Shahid and Glasser [21] presented accurate experimental results of the phase relations in the region at more than 50 wt% SiO$_2$ of the ternary system. The formation enthalpy and entropy of the ternary solid species were optimized following the phase fields and melting temperature accordingly. In the authors's previous study [6], equilibrium phase relations in the Na$_2$O-CaO-SiO$_2$ system at less than 50 wt% SiO$_2$ concentrations were experimentally investigated, and the primary phase field of compound Na$_2$Ca$_2$Si$_2$O$_7$ and four invariant points were given. The thermodynamic data of the solid species Na$_2$Ca$_2$Si$_2$O$_7$ and Na$_2$CaSiO$_4$ were optimized based on these experimental results [6].

In the present work the liquid surfaces were described by binary liquid species and their interaction relation. For the more than 50 wt% SiO_2 area, the thermodynamic data were assessed according to the phase fields and invariant points results. Experimental results of the pseudo-binary system Na_2SiO_3-$CaSiO_3$ were employed to refine the thermodynamic data of $Na_2Ca_2Si_3O_9$ and $Na_4CaSi_3O_9$ components. After the assessment, the new database including thermodynamic data and interaction parameters between species as listed in Table 1 and Table 2 was obtained. These data were collected from literature and optimized from original data as described in these two tables. Subsequently, the new optimized database was applied to calculate the phase diagrams.

4. Results and discussion

The calculated phase diagram for the Na_2O-SiO_2 system with the new optimized database and FACT database [11] is shown in Figure 1. The results indicate that the computed phase equilibria with new database are in good agreement with the experimental results. Morey and Bowen [17] studied the phase relations in the range between Na_2SiO_3 and SiO_2. Afterwards, Kracek [18] experimentally investigated the system with a bit more extensive rang to $Na_6Si_2O_7$ from SiO_2. The melting point of compound $Na_2Si_2O_5$ calculated in the present study is 878 °C which is a slightly higher than 873 °C as reported by Kracek [18]. Morey stated that Na_2SiO_3 melts congruently at 1086 °C. The present reproduced result is 1090 °C which is the same with Wu's assessment [22]. Loeffler [18] reported the compound $Na_6Si_2O_7$ congruently melting at 1115 °C and found two eutectics: between Na_4SiO_4 and $Na_6Si_2O_7$ (at 962 °C and 36.5 mol% SiO_2) and between $Na_6Si_2O_7$ and Na_2SiO_3 (at 1015 °C and 45.5 mol% SiO_2). In the present calculated phase diagram, the melting temperature of $Na_6Si_2O_7$ is 1110 °C, and the two eutectics in this research locate at 1010 °C and 36.5 mol% SiO_2 and 1021 °C and 44.5 mol% SiO_2, respectively. The two eutectics temperatures are ~50 °C and ~6 °C higher than the experimental results [18] respectively. $Na_6Si_8O_{19}$ was reported to melt incongruently at 809 °C to $Na_2Si_2O_5$ and liquid phase [20], which is predicted in the present work at 812 °C.
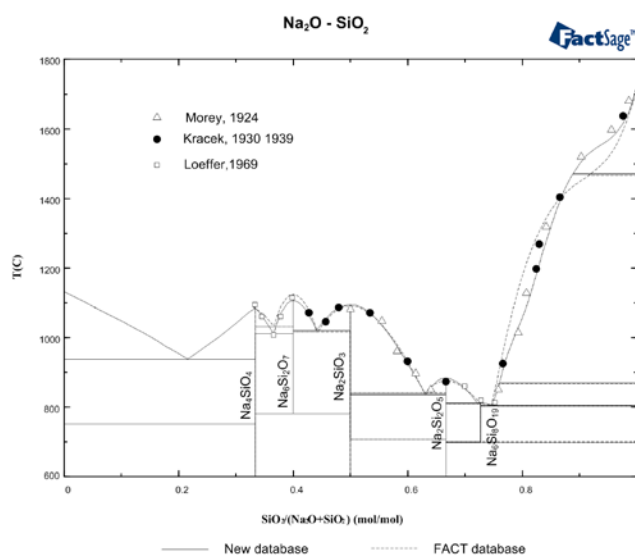
Fig .1 Phase diagram of Na_2O-SiO_2 system calculated with new database and FACT database

In general, the new optimized database can reproduce the phase equilibria in the binary system Na_2O-SiO_2 very well in the composition range from Na_4SiO_4 to SiO_2, especially in the SiO_2-rich region. This is attributed by the

incorporation of the optimized interaction parameters among the solution species. The modified associate species approach proves to be able to describe the phase relations in the whole composition range with better agreement to the experimental results. In the composition range from Na_4SiO_4 to silica the phase diagram is reproduced well by the FACT database. In the composition range from ~85 wt% to 100 wt% SiO_2 region, the results predicted by the FACT database are a little different from the present results.
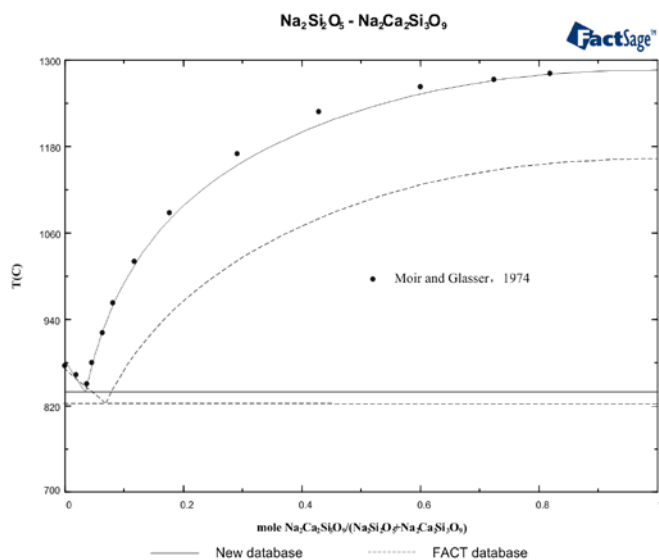
Fig. 2 Phase diagram of the system $Na_2Si_2O_5$- $Na_2Ca_2Si_3O_9$ calculated with new database and FACT database

In Moir and Glasser's work [23], the binary system Na_2SiO_3-$Na_2Ca_2Si_3O_9$ was investigated with high temperature equilibrium method. The eutectic point between these two compounds was determined at 5 mole% $Na_2Ca_2Si_3O_9$ and 840 °C. The calculated phase diagram with the new optimized database and the FACT database is shown as solid line and dash line in Figure 2, respectively. The calculated temperature with new database of the eutectic point is 830 °C which is 10 °C lower than the experimental result. The calculated phase equilibria with the FACT database are not comparable with the experimental results [23]. The liquidus surface calculated with the new database in the present study is in an acceptable agreement with Moir and Glasser's work [23].
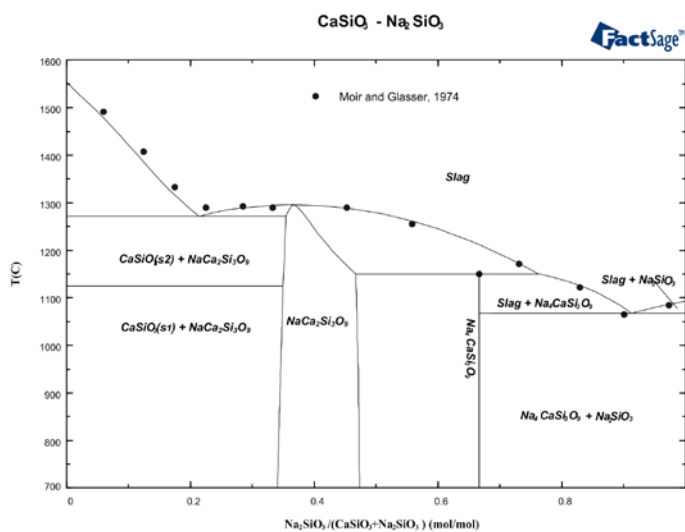
Fig. 3 Phase diagram of the system $CaSiO_3$-Na_2SiO_3 calculated with new database

The pseudo-binary system $CaSiO_3$-Na_2SiO_3 is very important for computing the phase relations in the CaO-SiO_2-Na_2O system. The phase equilibria of this pseudobinary system were experimentally studied by Moir and Glasser [23] with quenching method. They concluded that the phase field of $Na_2Ca_2Si_3O_9$ has a compositional range from 28.5 to 53.5±0.5 mol% Na_2SiO_3 at 1149 °C. However, it should be the solid solution of the compound $Na_2Ca_2Si_3O_9$ and $Na_4CaSi_3O_9$. Calculated phase diagrams of $CaSiO_3$-Na_2SiO_3 with optimized database in the present work is shown in Figure 3. It can be seen that the solid solution of the compound $Na_2Ca_2Si_3O_9$ and $Na_4CaSi_3O_9$ is described with the database as optimized in this study. The liquid surface in the whole compositional range is in an acceptable agreement with experimental results. The calculated melting temperature of $Na_2Ca_2Si_3O_9$ is 1285°C which is 4°C lower than the experimental value [23]. Because it is difficult to obtain reliable results, the calculated phase diagram of the binary system $CaSiO_3$-Na_2SiO_3 with the FACT database are not given in Figure 3.
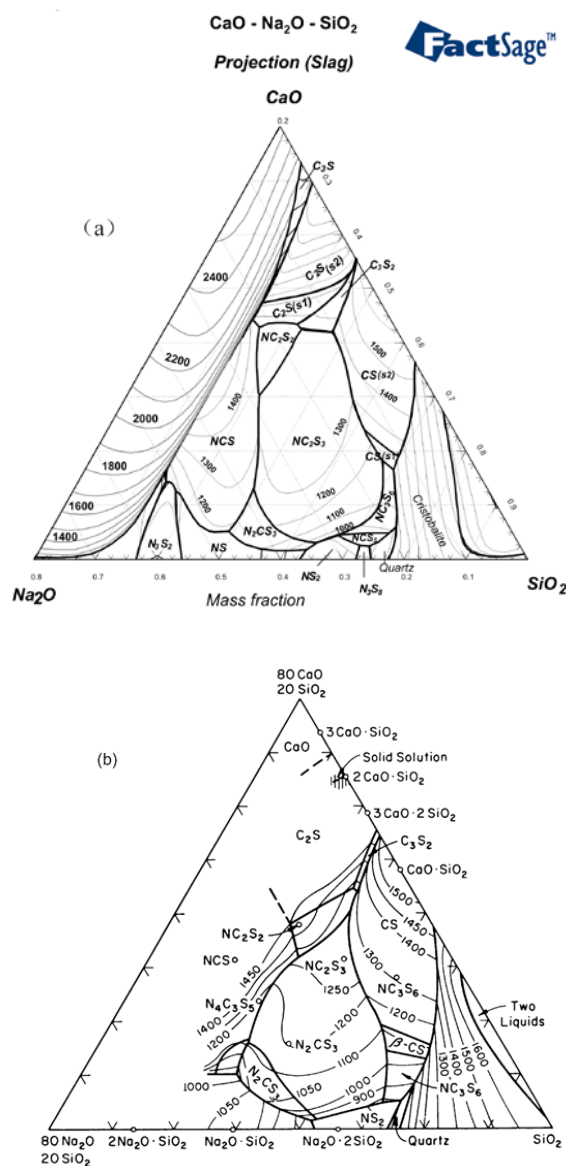
Fig. 4 Calculated phase diagram of the CaO—Na_2O—SiO_2 system (a) with the new database compared with experimental results (b) [20] (C=CaO; N=Na_2O; S=SiO_2).

Figure 4(a) and (b) show the calculated phase diagram of the ternary system CaO-SiO_2-Na_2O and the phase equilibria constructed based on the phase equilibrium experiments [20]. The phase field of, $CaSiO_3$ (CS) is reproduced well and is in good agreement with the experimental results. The phase fields of $Ca_3Si_2O_7$ (C_3S_2), Ca_2SiO_4 (C_2S) and $Na_2Si_2O_5$ (NS_2) are described not very well compared with experimental results, and they need to be further refined. In the region at more than 50 wt% SiO_2 of the ternary system, the $Na_2Ca_3Si_6O_{16}$ (NC_3S_6) and $Na_2CaSi_5O_{12}$ (NCS_5) phase fields are calculated, which is not in good agreement with experimental results. Comparing to the experimental results, the calculated $Na_2Ca_3Si_6O_{16}$ (NC_3S_6) phase field is in different shape, possibly due to the potential non-stochiometry solid solution of the phases $Na_4CaSi_3O_9$ (N_2CS_3). The boundary of the $Na_2Ca_3Si_6O_{16}$ (NC_3S_6) and $Na_4CaSi_3O_9$ (N_2CS_3) obviously needs more effort in optimization. The phase $Na_2CaSi_5O_{12}$ (NCS_5) fields and isotherms in this area are generated with slightly larger field area than reported by the experiments. The quartz and cristobalite phase fields are described in an acceptable agreement with the experimental results.

At less than 50 wt% SiO_2 of the CaO-SiO_2-Na_2O system, the calculated phase relations were compared to the experimental results [6, 20], and the predicted $Na_2Ca_2Si_2O_7$ (NC_2S_2) phase field is smaller. The ternary eutectic point of $Na_2Ca_2Si_3O_9$ (NC_2S_3), $Na_2Ca_2Si_2O_7$ (NC_2S_2) and Na_2CaSiO_4 (NCS) was experimentally determined to be at 1258 °C with a composition of 22.5 wt% Na_2O, 34.5 wt% CaO, and 43.0 wt% SiO_2 [6]. In the present modeling, the eutectic temperature of these three compounds was calculated as 1235°C with a composition of 28.0 wt% Na_2O, 31.0 wt% CaO, and 41.0 wt% SiO_2, and that is 23 °C lower than the measured value [6]. Eutectic reaction of phases $CaSiO_3$ (CS), $Ca_3Si_2O_7$ (C_3S_2) and $Na_2Ca_2Si_2O_7$ (NC_2S_2) at temperature 1270 °C has not been predicted in the present calculation. For the Ca_2SiO_4 (C_2S), $Ca_3Si_2O_7$ (C_3S_2) and $Na_2Ca_2Si_2O_7$ (NC_2S_2) phase fields, a peritectic point was established at 1251 °C with the compositions of 15.0 wt% Na_2O, 43.0 wt% CaO, and 42.0 wt% SiO_2 in the current computed phase diagram. However this peritectic point was determined at 1278 °C with 9.0 wt% Na_2O, 47.0 wt% CaO, and 44.0 wt% SiO_2 [6]. So far, the eutectic point of $CaSiO_3$ (CS), $Na_2Ca_2Si_3O_9$ (NC_2S_3) and $Na_2Ca_2Si_2O_7$ (NC_2S_2) phase fields has not yet been predicted in this study. The phase field of compound Na_2CaSiO_4 was predicted in the present phase diagram calculation. Due to the relative high temperature, this field was not well investigated completely in experimental work [20]. In general, the isothermal sections going through the phase fields of Na_2CaSiO_4 (NCS) and $Na_2Ca_2Si_2O_7$ (NC_2S_2) also need continuous effort for improvement.

5.   Conclusions

The ternary system CaO-SiO_2-Na_2O was thermodynamically evaluated with the modified associate species model. A new database has been constructed based on assessment on the sub-binary systems CaO-SiO_2 and Na_2O-SiO_2. The phase equilibria of these two binary systems can be well regenerated with the new database compared with experimental results. The phase relations of the pseudo-binary system $CaSiO_3$-Na_2SiO_3 were also reproduced well. In the computed phase equilibria of the system CaO-SiO_2-Na_2O, the binary phase fields were described and in agreement with the experimental results. In the composition region with more than 50 wt% SiO_2, the invariant points and ternary phase fields were predicted, and the phase fields of $Na_2Ca_3Si_6O_{16}$ and $Na_2CaSi_5O_{12}$ were not reproduced very well compared with experimental work. The phase fields of Na_2CaSiO_4 and $Na_2Ca_2Si_2O_7$ were predicted at compositions

with less than 50 wt% SiO_2, the liquidus surfaces and the isotherms in this area are not comparable with experimental results and need to be further optimized.

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