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A THERMODYNAMIC APPROACH TO THE CORROSION OF THE CATHODE REFRACTORY LINING IN ALUMINIUM ELECTROLYSIS CELL: MODELLING OF THE Al$_2$O$_3$-Na$_2$O-SiO$_2$-AlF$_3$-NaF-SiF$_4$ SYSTEM

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Abstract

The corrosion of the cathode refractory lining in electrolysis cells, partly due to the cryolite bath, can shorten the lifespan of the cell. This corrosion is usually studied with laboratory tests and cathode autopsies of shutdown cells, but the results might not correspond to the reactions taking place in service. The simplified corrosion problem (Al$_2$O$_3$-SiO$_2$ representing the aluminosilicate refractory, NaF-AlF$_3$ representing the cryolite bath) corresponds to the reciprocal system Al$_2$O$_3$-Na$_2$O-SiO$_2$-AlF$_3$-NaF-SiF$_4$. The thermodynamic modelling of this system permits the calculation of complex chemical equilibrium occurring at the service temperature. The reciprocal system has been assessed using the Modified Quasichemical Model in the Quadruplet Approximation (MQMQA), which takes into account both first-nearest-neighbour (FNN) and second-nearest-neighbour (SNN) short-range order (SRO) and allows the modelling of the strongly ordered oxyfluoride liquid solution. A unique set of model parameters is used to reproduce the experimental data. The results of the thermodynamic modelling of the Al$_2$O$_3$-Na$_2$O-SiO$_2$-AlF$_3$-NaF-SiF$_4$ system are presented here.

Introduction

Since Hall and Héroult both developed and patented a process for the production of aluminium in 1886, the method used for the electrolysis of alumina has not fundamentally changed [1]. In the last decades, efforts in research and development have permitted a better understanding of the different phenomena and properties (MHD, bath chemistry and physical properties, thermodynamic modelling...) and improvements to the process and cell operations (higher current intensity, better quality of the alumina feed, improved carbon materials for the cathode...). The lifespan of the cell and the production efficiency have increased [1]. The lifespan of the cell depends, among others [1], on the cathode life time (in average between 1800 and 2800 days [2] for modern cells, but can extend to more than 4000 days). The large variation for cathode life time (even for cells of the same design) indicates the impact of the cell operation [2]. The cell temperature and the heat balance are very important parameters to control. To maintain these operation parameters as steady as possible, the refractory lining plays an important role, and must keep its thermo-mechanical properties despite being exposed to the cryolite bath, sodium or aluminium. Degradation of the refractory lining usually results in increased heat losses, which induce higher energy consumption [3]. In some cases, the interactions between the penetrating liquids and the refractory lining may results in a complete cathode block failure [3] which forces the shutdown of the cell. The costs of relining, for large modern cells, are estimated to exceed 100,000 $US [2] (approximately 300,000$US in 2011 for a 350 to 450 kA

modern cell). Cells with a short lifespan have economic consequences for the aluminium producers. The choice of materials used for the cathode refractory lining is therefore really important and should take into account the recent developments of the cell in order to have the required properties. Reviews of refractory materials used in electrolysis cells, different requirements for their properties and characterisation techniques have been presented [4; 5].

Understanding the different mechanisms involved in the degradation of materials of the cathode refractory lining [1; 6-8] is necessary to insure that these materials will be able to perform as designed during the lifespan of the cell. The degradation of the refractory materials, also referred as corrosion, is usually studied either through laboratory tests [9-12] or with cathode autopsies of shutdown cells [13-18]. Based on the phase equilibria observed for different corrosive agents, a unified approach of the corrosion of the refractory lining was proposed by Pelletier et al. [19] which allows some prediction of in-service behaviour. However, this unified approach does not include a thermodynamic model allowing the calculation of the complex chemical equilibrium involved, but is based on reported phase diagrams [6; 20] in the Al$_2$O$_3$-Na$_2$O-SiO$_2$-AlF$_3$-NaF-SiF$_4$ system. Additionally, Tschope et al. [21] recently pointed out that the observations made on shutdown cells might not reflect the situation in the cathode refractory lining while in-service.

In the present work, the corrosion of the refractory materials is considered from a thermodynamic point of view. The underlying hypothesis is, provided that the oxyfluoride liquid solution, the solid solutions, the stoichiometric solids and the gas phase are modeled in the Al$_2$O$_3$-Na$_2$O-SiO$_2$-AlF$_3$-NaF-SiF$_4$ quaternary reciprocal system and reproduce the experimental data, it will be possible to calculate thermodynamic equilibrium or metastable equilibrium corresponding to different local conditions in the cathode refractory lining. The thermodynamic calculations may permit the prediction of chemical reactions occurring in the refractory materials for a set of conditions corresponding to in-service situations.

Few thermodynamic models have been applied successfully to oxyfluoride melts [22-25]. These models are generally restricted both in composition and in temperature because of the difficulty to reproduce the non-ideality and the configuration of the species in these melts. In previous assessments [26; 27], the MQMQA has been successfully used to reproduce the thermodynamic properties of the strongly ordered oxyfluoride melt in subsystems of the Al$_2$O$_3$-Na$_2$O-SiO$_2$-AlF$_3$-NaF-SiF$_4$ system.
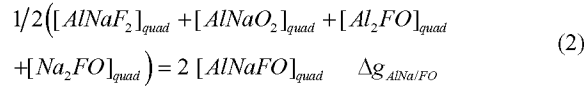
Thermodynamic Modelling

The MQMQA [28] is a two-sublattice model which takes into account short-range order. The quadruplets considered in the

model are constituted from two cationic and two anionic species and are not meant to be real structural entities, but rather a simplified way of considering simultaneously FNN and SNN pairs. Two species from different sublattices are FNN, and two species from a same sublattice are SNN. For each species within a quadruplet, a SNN coordination number is required. SNN coordination numbers are not meant to represent the physical coordination of the ions in the liquid phase but are rather model parameters which can be adjusted in order to set the composition of maximum SRO in the binary and reciprocal systems.

End-members of the liquid solution, *i.e.* Na$_2$O, NaF, AlF$_3$, Al$_2$O$_3$, etc. are represented by unary quadruplets, respectively [Na$_2$O$_2$]$_{quad}$, [Na$_2$F$_2$]$_{quad}$, [Al$_2$F$_2$]$_{quad}$, [Al$_2$O$_2$]$_{quad}$, etc. The Gibbs energy function of the unary quadruplets are related to the Gibbs energies of the corresponding pure liquid via the SNN coordination numbers. In binary systems, interactions between species in the liquid phase are modeled through a formation reaction of a binary quadruplet from the unary quadruplets:

$$\left[Na_2O_2\right]_{quad} + \left[Al_2O_2\right]_{quad} = 2\left[AlNaO_2\right]_{quad} \quad \Delta g_{AlNa/O_2} \quad (1)$$
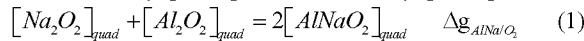
Similar reactions can be written for all the binary systems. No additional quadruplets are considered in ternary or higher order non-reciprocal systems. In reciprocal systems, a formation reaction of a reciprocal quadruplet from the binary quadruplets is considered:

$$1/2\left([AlNaF_2]_{quad} + [AlNaO_2]_{quad} + [Al_2FO]_{quad}\right.$$
$$\left. + [Na_2FO]_{quad}\right) = 2\,[AlNaFO]_{quad} \quad \Delta g_{AlNa/FO} \quad (2)$$

In reciprocal systems, the extent of SRO between FNN ions is related to the exchange reaction between the end-members, for example in the Al$_2$O$_3$-Na$_2$O-AlF$_3$-NaF ternary reciprocal system:

$$3\,Na_2O + 2\,AlF_3 = 6\,NaF + Al_2O_3 \quad \Delta g^{exchange} \quad (3)$$
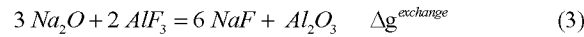
The different Gibbs energies used in the MQMQA and the relations between them have been previously described in details by Pelton et al. [28]. The Gibbs energy changes related to the formation reactions of the binary and reciprocal quadruplets, reactions (1) and (2), are adjustable model parameters used to reproduce the experimental data. The properties of the liquid solution in a multicomponent system are adjusted with the extrapolation of binary parameters system in common ion and reciprocal systems, as described in [29], and with ternary parameters if necessary.

The quadruplets are mixing randomly on "quadruplet sites", and the equilibrium quadruplet composition is calculated by minimizing the Gibbs energy of the solution with respect to the elemental balance. The Gibbs energy of the liquid solution is given by the model as follows:

$$G = \sum_{i=cations} \sum_{j=cations} \sum_{k=anions} \sum_{l=anions} n_{ij/kl}g^{\circ}_{ij/kl} - T\Delta S^{config} \quad (4)$$

where $n_{ij/kl}$ is the number of moles of the *ij/kl* quadruplet, $g^{\circ}_{ij/kl}$ its Gibbs energy and ΔS^{config} is the configurational entropy. No exact mathematical expression is known for ΔS^{config}, which is related to the distribution of the quadruplets over the "quadruplet sites", and the configurational entropy has been approximated by Pelton et al. [28]. Recent improvements of this approximation have been made by Pelton et al. [30] and presented elsewhere [26]. Calculations are performed with the FactSage™ thermochemical software [31].

Results

The Al$_2$O$_3$-Na$_2$O-SiO$_2$-AlF$_3$-NaF-SiF$_4$ quaternary reciprocal system is constituted from nine binary systems, two ternary systems and three ternary reciprocal subsystems. Some of these subsystems are key systems for numerous scientific and technological fields, and have been extensively studied. However in other subsystems, there is a partial or total lack of thermodynamic and phase equilibrium data, making difficult the thermodynamic modelling of these subsystems. When available, all types of experimental data have been taken into account (enthalpies, partial pressures, *emf*, phase equilibrium, liquidus, etc.). The detailed assessments of the Na$_2$O-SiO$_2$-NaF-SiF$_4$ and Al$_2$O$_3$-SiO$_2$-AlF$_3$-SiF$_4$ ternary reciprocal system have been previously presented [26; 27]. Here are presented some selected results for some of the subsystems.

Binary systems

In the case of five of the nine binary systems, experimental data could be used to optimise the model parameters for these systems. No or insufficient data were available for the AlF$_3$-Al$_2$O$_3$, AlF$_3$-SiF$_4$, NaF-Na$_2$O and SiF$_4$-SiO$_2$ binary systems, and ideal mixing was assumed in the liquid phase.

The Al$_2$O$_3$-Na$_2$O system

The Al$_2$O$_3$-Na$_2$O binary system [32-41] is a key system for the aluminium industry, and some intermediate compounds, *i.e.* NaAl$_{11}$O$_{17}$ (β-Al$_2$O$_3$), are likely to be formed in the case of the corrosion of the refractory lining [3; 20].
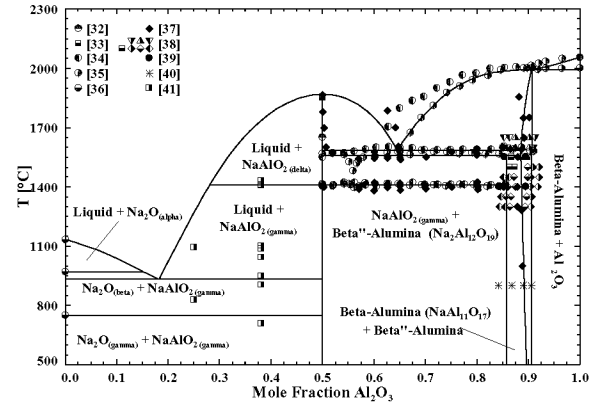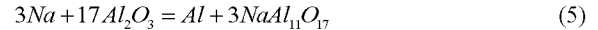
Figure 1. Calculated Na$_2$O-Al$_2$O$_3$ phase diagram.

With the thermodynamic model, the reactions occurring when alumina is exposed to vapours of Na, such as the formation of sodium aluminates, can be predicted:

$$3Na + 17Al_2O_3 = Al + 3NaAl_{11}O_{17} \quad (5)$$

Phase equilibrium for Al$_2$O$_3$ exposed to Na is shown in Figure 2.
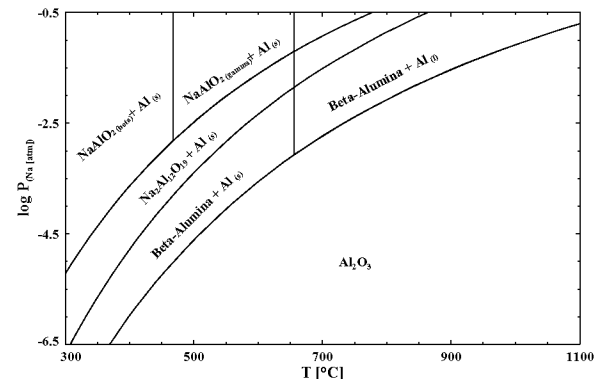
Figure 2. Phase equilibrium for Al_2O_3 exposed to Na.

The Al_2O_3-SiO_2 system

Mullite, $Al_6Si_2O_{13}$, is an important compound for the refractory materials. The mullite solid solution model used in the work was described in [42]. Model parameters for the liquid solution were optimised to reproduce the liquidus and the mullite solubility limits data [43-64].
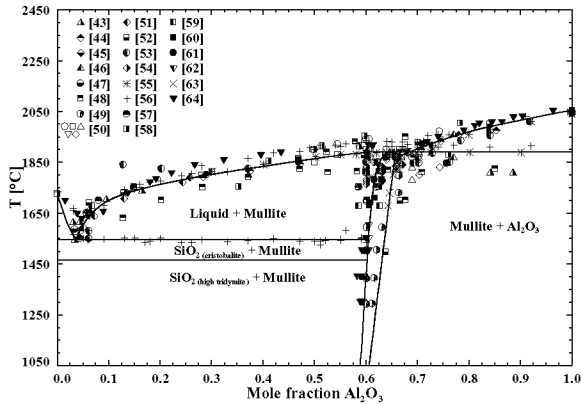
Figure 3. Calculated Al_2O_3-SiO_2 phase diagram.

The Na_2O-SiO_2 system

The Na_2O-SiO_2 system has been extensively studied and numerous thermodynamic data are available [36; 41; 65-80]. All data have been considered, and a unique set of binary parameters for the liquid solution was optimised to reproduce the experimental data considered reliable.
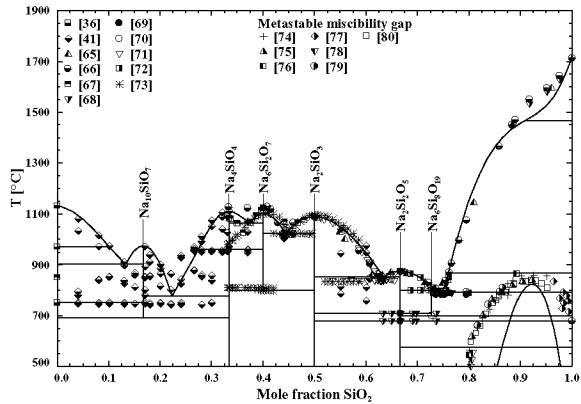
Figure 4. Calculated Na_2O-SiO_2 phase diagram.

The NaF-SiF_4 system

The estimation for the hypothetical high-temperature liquid SiF_4, necessary to model the liquid solution, and the details of the assessment are presented in [26] and the phase diagram [81; 82] is shown in Figure 5. Malladrite, Na_2SiF_6, is the only intermediate compound in this system, which has also been reported in cathode autopsy [14].

The NaF-AlF_3 system

The NaF-AlF_3 system has been previously optimised by Chartrand and Pelton [24], and their model parameters for the liquid and

solid cryolite solutions have been used in the present work. Thermodynamic calculations in the NaF-AlF_3 system will give identical results as obtained by Chartrand and Pelton [24].
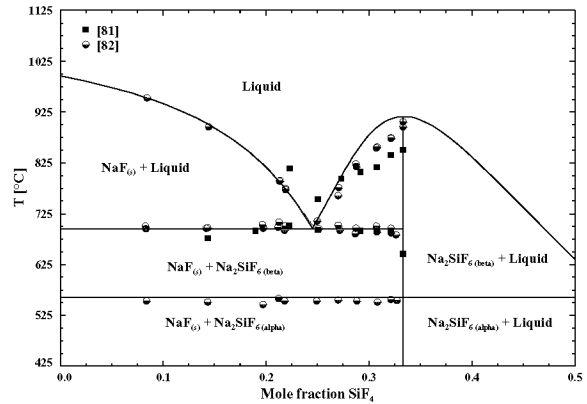
Figure 5. Calculated NaF-SiF_4 phase diagram.

Ternary systems

Two ternary systems are considered in this work. The oxide ternary system is of importance for metallurgical, geophysical and glass applications, and has been studied in details. Only scarce experimental data [83] are available for the AlF_3-NaF-SiF_4 ternary system, the model is then purely predictive.

The Al_2O_3-Na_2O-SiO_2 system

The oxide ternary system, Al_2O_3-Na_2O-SiO_2, has been mainly studied in the SiO_2-rich region, and data in different pseudo-binary systems have been reported [33; 84-88]. However, liquidus data for low SiO_2 content have only been reported by Schairer and Bowen [33] and additional data would be required to improve the thermodynamic modelling in the Al_2O_3-$NaAlSiO_4$-Na_2O region.
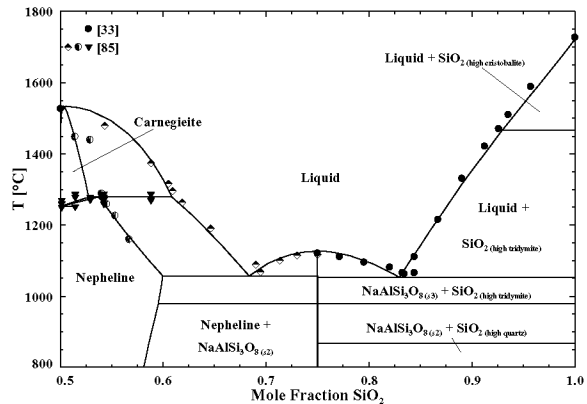
Figure 6. Calculated $NaAlO_2$-SiO_2 phase diagram.

Reciprocal systems

The AlF_3-NaF-Al_2O_3-Na_2O system

This ternary reciprocal system has been previously modeled, in the region of interest for the aluminium industry, by Chartrand and Pelton [24], who have considered most of the experimental data. Contrary to the NaF-AlF_3 system, their reciprocal model parameters (Eq. (2)) have not been used here because different model parameters are used in this work for the Al_2O_3-Na_2O

system. Agreement with the experimental data obtained in this work is similar as obtained by Chartrand and Pelton [24], for example in the Na_3AlF_6-Al_2O_3 isoplethal section [89-110].
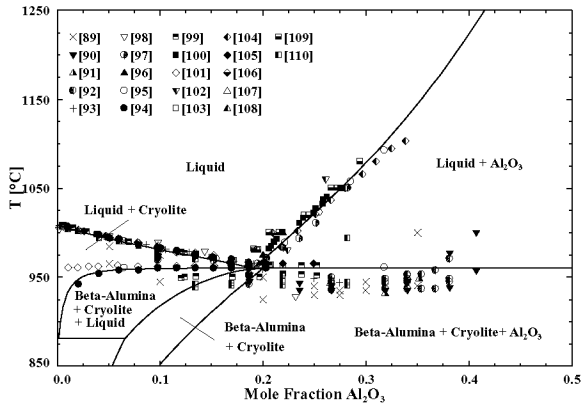

Figure 7. Calculated Na_3AlF_6-Al_2O_3 phase diagram.

The NaF-SiF$_4$-Na$_2$O-SiO$_2$ system

Liquidus data have only been measured in different isoplethal sections [23; 71; 111-113] of the NaF-Na$_2$O-SiO$_2$ subsystem due to the experimental challenges related to the relatively high SiF$_4$ partial pressure at high SiF$_4$ content. Some experimental data [113] are in conflict and have not been taken into account [26].
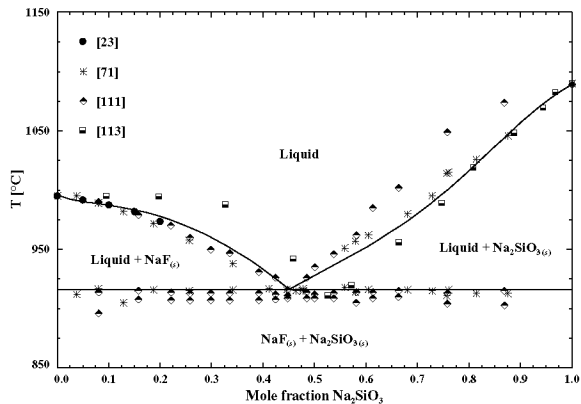

Figure 8. Calculated NaF-Na$_2$SiO$_3$ phase diagram.

The AlF$_3$-SiF$_4$-Al$_2$O$_3$-SiO$_2$ system

Few data [114; 115] have been reported for isoplethal sections in the ternary reciprocal system. The reciprocal compound fluor-topaz has been characterized [116] and previously modeled [27]. Isotherms at six different temperatures have been previously presented [27] which show the different solid-solid and solid-gas phase equilibrium in the AlF$_3$-SiF$_4$-Al$_2$O$_3$-SiO$_2$ system.

The AlF$_3$-NaF-SiF$_4$-Al$_2$O$_3$-Na$_2$O-SiO$_2$ system

The quaternary reciprocal system has mainly been studied in regards with the corrosion of the cathode refractory lining. The reported liquidus and phase equilibrium data [6; 20; 117-119] are usually in isoplethal sections between a composition in the AlF$_3$-NaF system and a composition in the Al$_2$O$_3$-Na$_2$O-SiO$_2$ system.

Discussion

The design of the cathode refractory lining requires knowing how the refractory materials will resist to the different corrosive agents during the life of the cell. However during the cell operations, the conditions to which the refractory materials are exposed may vary significantly. Temperatures variations, shifts in chemical composition, exposure to different corrosive agents, etc. will affect the refractory materials. The corrosion of the refractory lining in electrolysis cells depends on thermodynamic and kinetic aspects (related, among others, to physical properties, porosity and transport phenomena). Reported corrosion products (observed at room temperature) are almost all equilibrium phases [19; 20] apart from glassy phases (corresponding to the liquid cooled from in-service temperature).
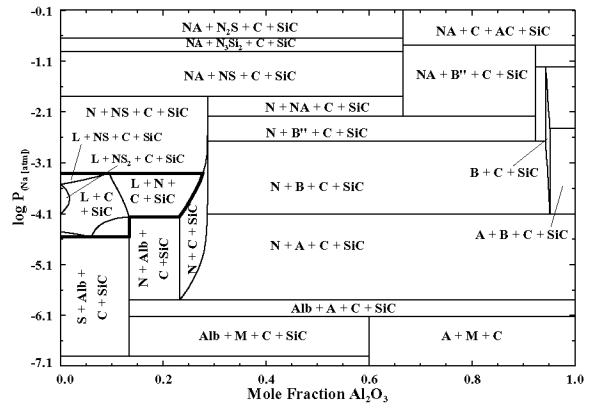

Figure 9. Phase equilibrium vs. Na partial pressure in the Al_2O_3-SiO_2 system at 850°C at C saturation (A=Al_2O_3, AC=Al_4C_3, Alb=Albite, B=β-Al_2O_3, B''=β''-Al_2O_3, L=Liquid, M=Mullite, N=Nepheline, N_2S=Na_4SiO_4, N_3S_2=$Na_6Si_2O_7$, NS=Na_2SiO_3, NS_2=$Na_2Si_2O_5$, S=SiO_2).

Therefore, with a properly calibrated thermodynamic model for the Al-Na-Si-NaF-AlF$_3$-SiF$_4$-Na$_2$O-Al$_2$O$_3$-SiO$_2$-(C) system, predicting the effect of corrosion would be mainly related to predicting the role of the kinetic aspects (mostly heat and mass transfers) constrained by the cell design, and local phase equilibrium could be obtained by thermodynamic calculations for the local conditions (see Figure 9 and 10).
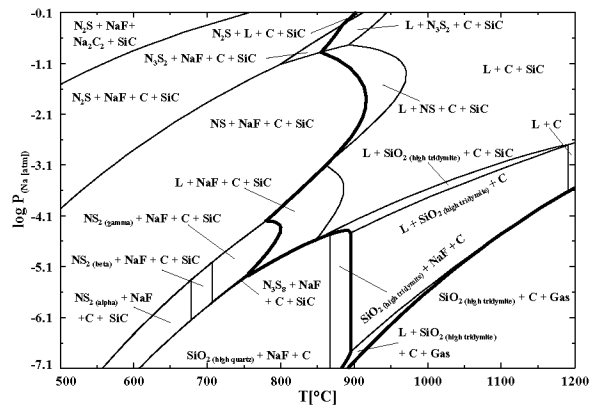

Figure 10. Phase equilibrium vs. Na partial pressure for SiO$_2$ in presence of NaF at C saturation (L=Liquid, N_2S=Na_4SiO_4, N_3S_2=$Na_6Si_2O_7$, NS=Na_2SiO_3, NS_2=$Na_2Si_2O_5$, N_3S_8=$Na_6Si_8O_{19}$).

The presence of other oxides in the refractory materials, for example CaO or oxide phases containing Ca, as well as minor oxide impurities, will require an extension of the thermodynamic model developed in this work, which will permit calculations for refractory materials similar to the industrial cathode lining.

Conclusion

The thermodynamic properties of the oxyfluoride liquid solution have been modelled with the MQMQA [28] as well as the solid solutions and the stoichiometric compounds in the AlF_3-NaF-SiF_4-Al_2O_3-Na_2O-SiO_2 quaternary reciprocal system. The model permits the calculation of thermodynamic or metastable phase equilibria. Based on these calculations, the behaviour of aluminosilicate refractory, when exposed to corrosive agents in conditions similar to the in-service conditions, may be estimated.

Acknowledgments

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