# Thermodynamic Assessment of the Alumina-Sodium Oxide-Silica using the Modified Quasichemical Model

Guillaume LAMBOTTE *(PhD Student)* and Patrice CHARTRAND *(Professor)*
**C**entre for **R**esearch in **C**omputational **T**hermochemistry (CRCT)
École Polytechnique de Montréal
**Info:** *guillaume.lambotte@polymtl.ca*

## Abstract

**F**or the production of aluminum electrolytic cells are used (Fig. 1), in which the electrolysis of alumina ($Al_2O_3$) dissolved in a cryolitic ($Na_3AlF_6$) based bath is done at around 4.2 V and 300 kA.

**A**ccording to Øye & al. if the chemical erosion of the carbon cathode block ($Al_4C_3$ formation and dissolution) was the only failure of the cell, then it could operate around 11 years. However it is never the case in the industry because failure due to corrosion of the refractory layers is the most common reason for cell shut down.

**I**n the cell the refractory lining is mainly composed of aluminosilicate materials. The corrosion of this lining is due to the penetration of bath and aluminum through the carbon cathode block. Different corrosion mechanisms are involved which will lead to the progression of the corrosive media further in the refractory layer.

**P**ost-mortem analysis (Fig. 2), is so far the best solution to understand the mechanism of corrosion, but is based on an analysis of the phases observed at room temperature after the cell shut down.

**P**redicting the corrosion reactions and the corrosion products at operating temperatures (around 960ºC) will be a great advantage to the industry, resulting in a better design of cell refractory lining in order to resist corrosion, have longer lifespan and more stable thermal and mechanical properties.

**A** CALPHAD type modeling forms the backbone of such a prediction tool. Thermodynamic software will provide the equilibrium calculation tool.

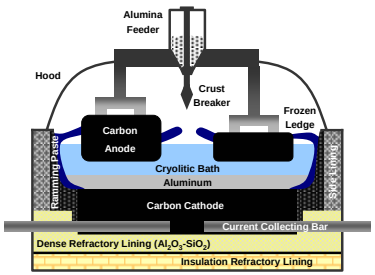



*Fig. 1: Schematic view of an aluminum electrolysis cell*

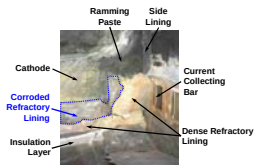



*Fig. 2: Post-mortem analysis of an aluminum electrolysis cell*
(source: http://www.ceramics-research.com)

## Thermodynamic Modeling

**T**he chemical system corresponding to the simplified problematic of the corrosion of aluminosilicate refractory materials by the cryolitic bath is the Al, Na, Si // F, O reciprocal system (Fig. 3). Interactions with carbon, sodium and aluminum are also to be taken into account.

**T**he NaF-$AlF_3$ join represents the cryolitic bath, and the aluminosilicate refractory lining has its composition along the $Al_2O_3$-$SiO_2$ join.

**T**he special features of this system are:

- Strong short range order in the liquid phase
  - ✓ In the binary subsystems $Na_2O$-$SiO_2$ and $Na_2O$-$Al_2O_3$.
  - ✓ Charge compensation effect in the silica-rich region of the liquid slag (replacement of a tetrahedral $Si^{4+}$ by a tetrahedra formed by an $(Na\text{-}Al)^{4+}$ pair in the silicon network).
- Limited solid solubilities.
- Metastable miscibility gaps in the molten oxides (of technological importance for ceramic industry).
- Stable miscibility gaps in the oxifluoride melts.

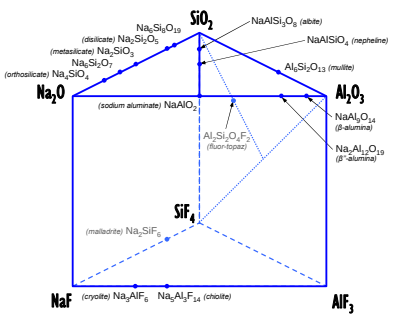



*Fig. 3: Al, Na, Si // F, O Reciprocal system*

**S**trong interactions are observed between the components, both in the solid and liquid states, resulting in strong short range order in the liquid solution: second nearest neighbour cationic ordering is modeled using the Modified Quasichemical Model in the Quadruplet Approximation (MQMQA). However in order to model the complete composition of the system we need to take into account anion interactions (mixing of $O^{2-}$ and $F^-$ on the second sublattice).
MQMQA : 2 sublattice model

- Components : cation sublattice Al, Na, Si, anion sublattice F, O.
- Quadruplets : unary Al–F, Si–O … binary Al–F, Si–O … reciprocal Al–F, Si–O …
- Gibbs energy :
  from pure component, $Al_2O_3$ Al–O, NaF Na–F …; binary system, $Na_2O$-$SiO_2$ Si–O …; reciprocal system $AlF_3$-NaF-$Al_2O_3$-$Na_2O$ Al–F …
- Quadruplets mix randomly with overlapping of pairs and ions (the configurational entropy term take this into account).
- Equilibrium is obtained by Gibbs energy minimization constrained by an elemental mass balance.

**T**he first step in the thermodynamic modeling of this reciprocal system is to obtain model parameters for the $Al_2O_3$-$Na_2O$-$SiO_2$ system. In the case of the oxide subsystem we only have one anion mixing on the second sublattice. Second nearest neighbour coordination numbers have to be defined which allow to reproduce the composition of the maximum short-range ordering in the different subsystems. To model the charge compensation effect we have introduced a $NaAl^{4+}$ associate, which will mix on the cation sublattice.

## Binary Systems

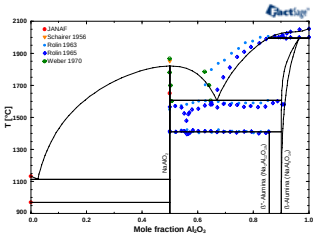
**A** critical review of the available data for the binary, ternary and reciprocal subsystems has been performed, and the data are being used in the on-going optimization process. The presented figures represent the work in progress.

**T**he ordering compositions in the liquid phase are set to the following composition in the different binary subsystems:

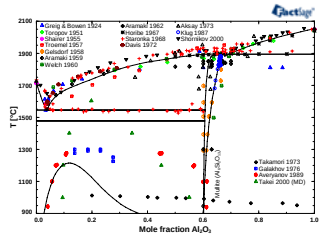
- $Al_2O_3$-$Na_2O$: we have decided to extend the stability of the associate $NaAl^{4+}$ from the ternary into the binary system in order to optimize it while maintaining cation distribution in the reciprocal system.
- $Al_2O_3$-$SiO_2$: at the mullite (3 $Al_2O_3$,2 $SiO_2$) composition $X_{Al2O3}$=0.6 .
- $Na_2O$-$SiO_2$: at the orthosilicate composition, $Na_4SiO_4$ or $X_{Na2O}$=0.8 .

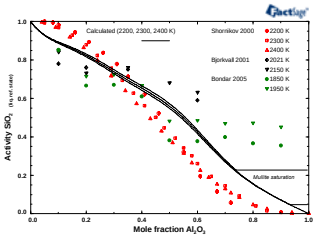
**T**hermodynamic properties of solids are mainly based on JANAF and Barin thermodynamic tables and the previous optimization of the system by P. Wu (PhD Thesis, CRCT, 1993)

- $Al_2O_3$-$Na_2O$

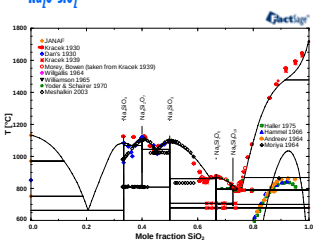


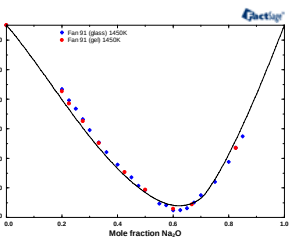

- $Al_2O_3$-$SiO_2$

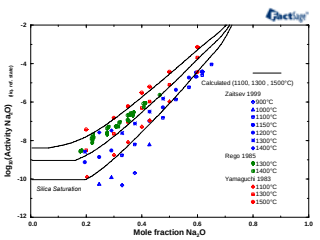


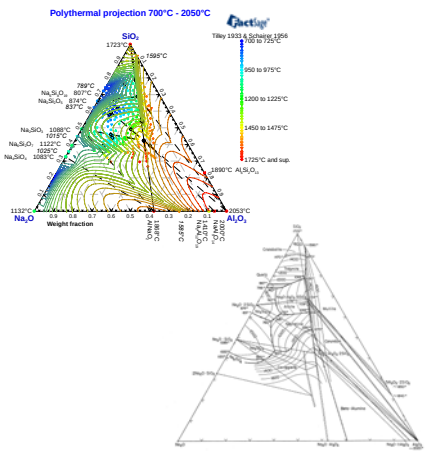

- $Na_2O$-$SiO_2$



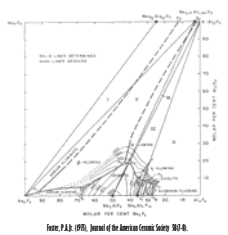




## Ternary System

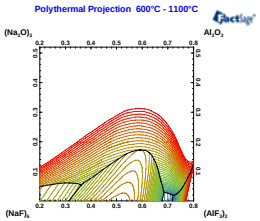



## Reciprocal System

**O**ptimization of the NaF-$AlF_3$-$Al_2O_3$ subsystem has already been performed (P. Chartrand, 2002). The integration of this previous work to our optimization of the oxide subsystem and the further optimization of the reciprocal system should be done without major changes.



Foster, P.A.Jr. (1958), Journal of the American Ceramic Society 30:53-60.




E.F. Osborn and A. Muan (1964), extracted from Phase Diagram for Ceramists, fig. 1-130, The American Ceramic Society.

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