Thermodynamic assessment of platinoid and molybdate phases in nuclear waste glasses

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Background of the study: Vitrification of the nuclear high level wastes

Fission products and actinides arising from the spent UOX fuel reprocessing are vitrified in borosilicate glasses. Among the fission products, platinum-group metals (Pd-Rh-Ru) exhibit very low solubility and partly precipitate as metal or oxide phases in the melt, molybdenum interacts with the glass frit to form molybdate phases known to precipitate as a complex phase called "yellow phase". These platinoid and molybdate phases may induce modifications of the physico-chemistry of the glass melt and alter the final glass confinement properties. To understand the relative stability of these phases depending on both temperature and oxygen potential of the melt, a thermodynamic database is being developed using the Calphad method.

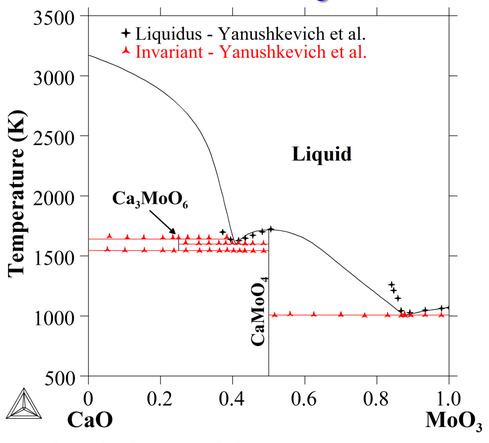
To consider the formation of molybdates, the CaO-MoO_3 and the Na_2O-MoO_3 pseudo-binary systems are assessed. The modeling of the Na_2O-SiO_2, MoO_3-SiO_2 and of the ternary SiO_2-Na_2O-MoO_3 system was carried out based on the literature and on new experiments in order to consider a simplified glass melt. Furthermore, the developed database includes the metallic and oxide complex platinoid system and some of the interactions with selenium and tellurium: Pd-Rh-Ru-Se-Te-(O).

Using this tool, the thermodynamic behavior of the platinoid and molybdate phases is calculated as a function of temperature and composition. This study throws new light on the interactions between poorly soluble fission products and the glass melt during the vitrification process of high level nuclear wastes.

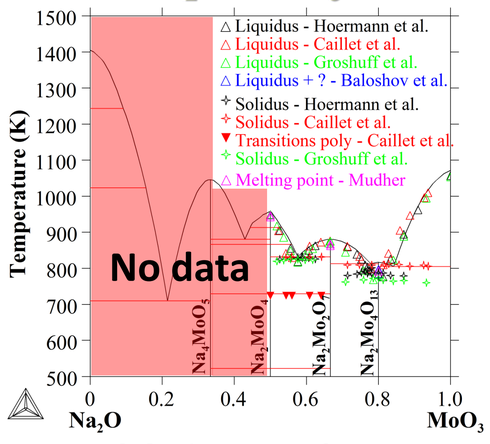
Results of the modeling

Molybdate and simplified glass melt phase diagrams

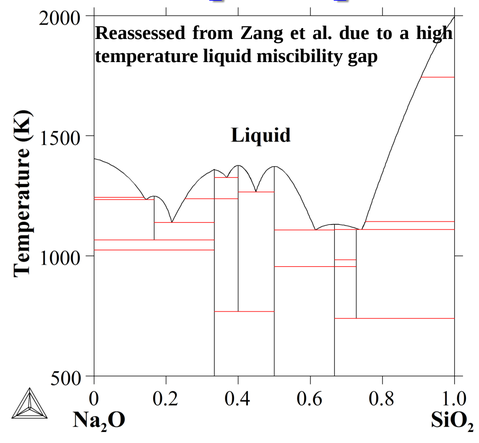
CaO-MoO_3



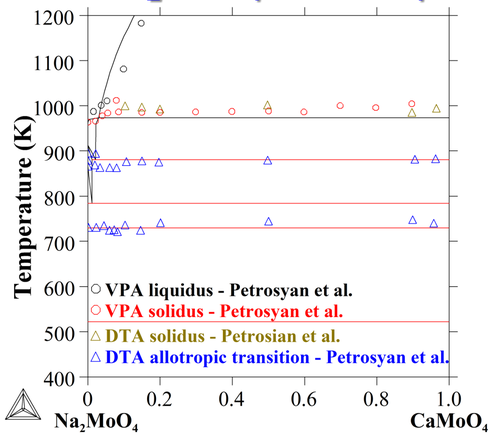
Na_2O-MoO_3

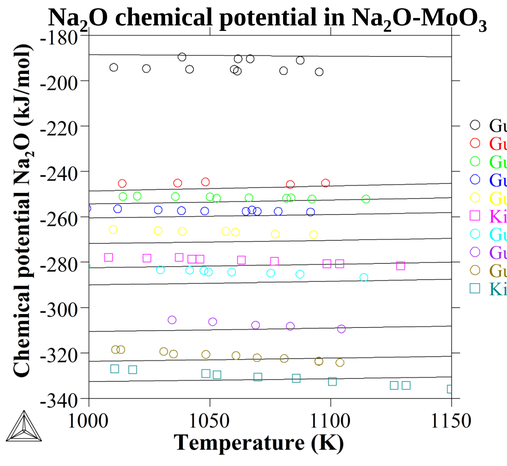


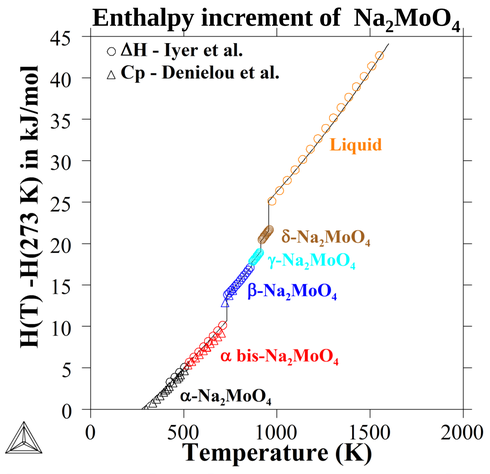
Na_2O-SiO_2

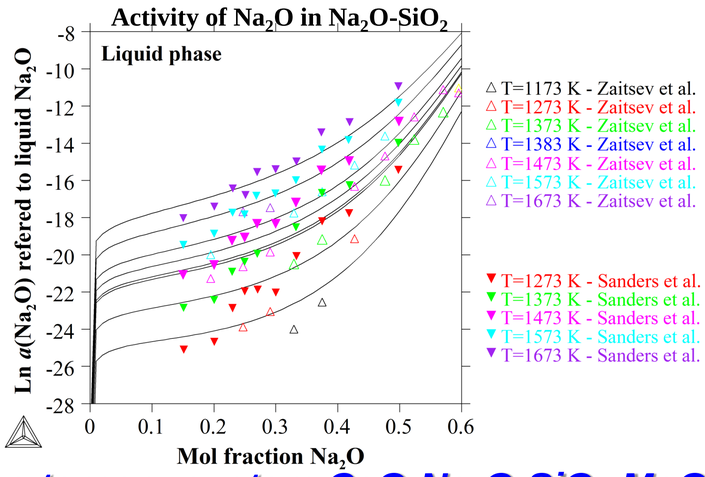


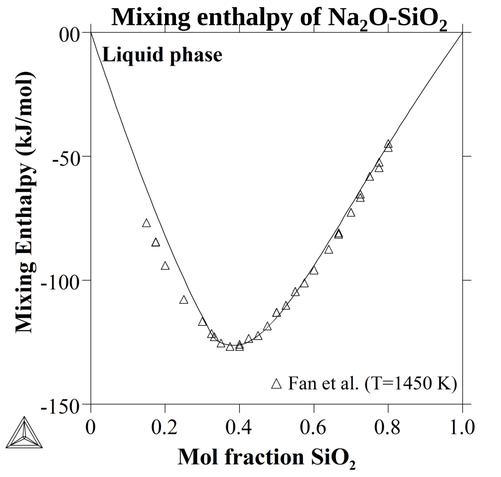
Na_2MoO_4-$CaMoO_4$









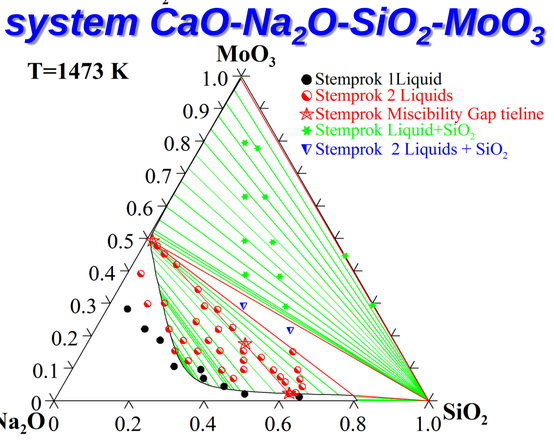


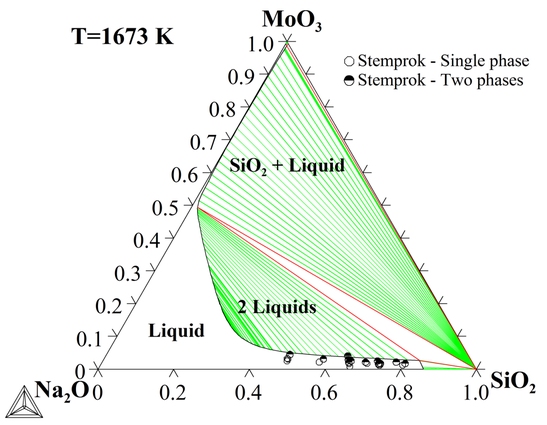
Molybdate/Glass melt phase separation: the ternary system CaO-Na_2O-SiO_2-MoO_3

Demixing phenomena of molybdate phases in a glass melt
Courtesy of Sophie Schuller, CEA Marcoule

Pouring of inactive glass melt
CEA Marcoule

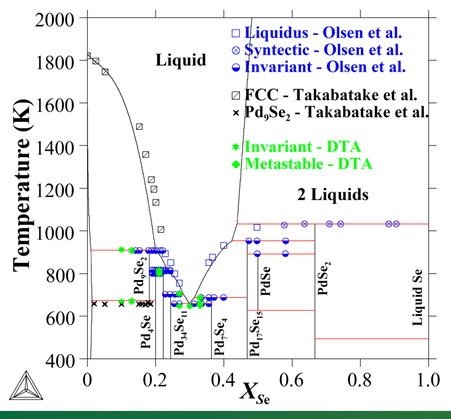
The CaO-Na_2O-SiO_2-MoO_3 system is a simplified melt representative for the industrial glass melt.
Thermodynamic calculations will make it possible to predict the high temperature behavior of molybdate phases during the vitrification process of nuclear wastes



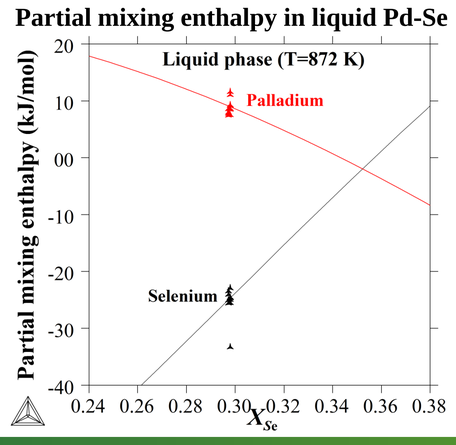


Platinoids

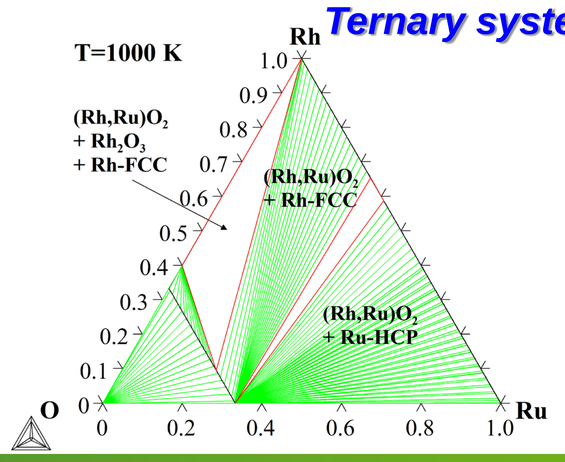
Pd-Se

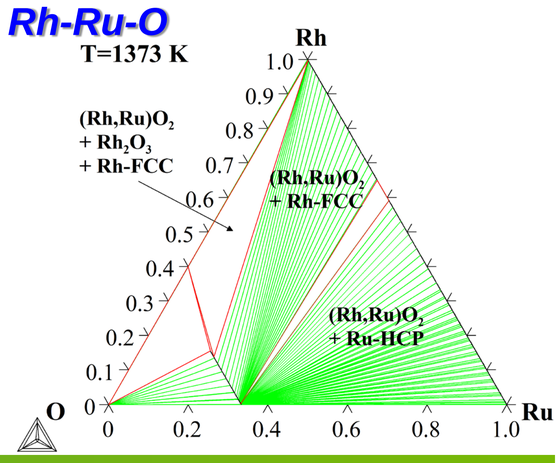


Partial mixing enthalpy in liquid Pd-Se



Ternary system Rh-Ru-O





Conclusions and prospects

The modeling of CaO-MoO_3, Na_2O-MoO_3, Na_2MoO_4-$CaMoO_4$ and of SiO_2-Na_2O-MoO_3 systems has been carried out. This study makes it possible to predict the formation of the molybdate phases in the simplified glass melt. The next step will focus on the introduction of B_2O_3 in the database to get closer to the real industrial glass composition.

The Pd-Se and Pd-Te systems have been modeled. An assessment of the Pd-Se-Te system will be available soon. In parallel, the Rh-Ru-O database enables to calculate the speciation of the platinoids in the glass as a fuction of oxygen potential and temperature.

This work will help to predict the high temperature interactions between some poorly soluble fission products (Mo, Pd, Rh, Ru) and the glass melt during the vitrification process, of nuclear wastes