Thermodynamic modelling of key metallic sub-systems for the treatment of mid-level wastes

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SERVICE OF CORROSION AND MATERIALS BEHAVIOUR IN THEIR ENVIRONMENT

Thermodynamic modelling of key metallic sub-systems for the treatment of mid-level wastes

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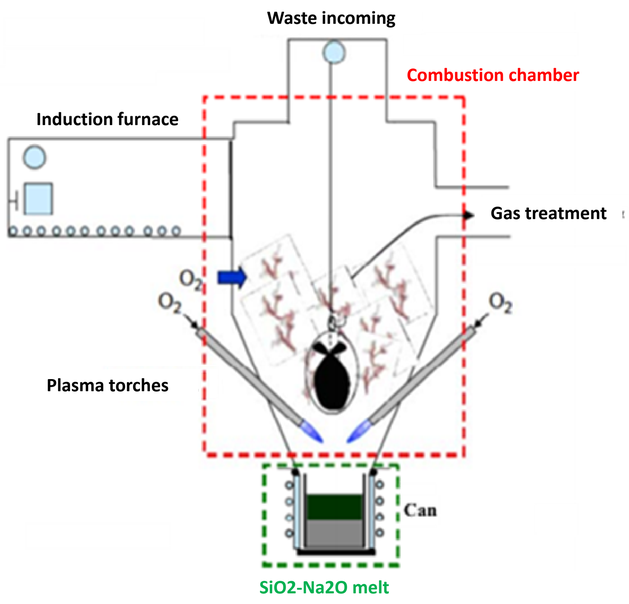
Context and Aim of the work

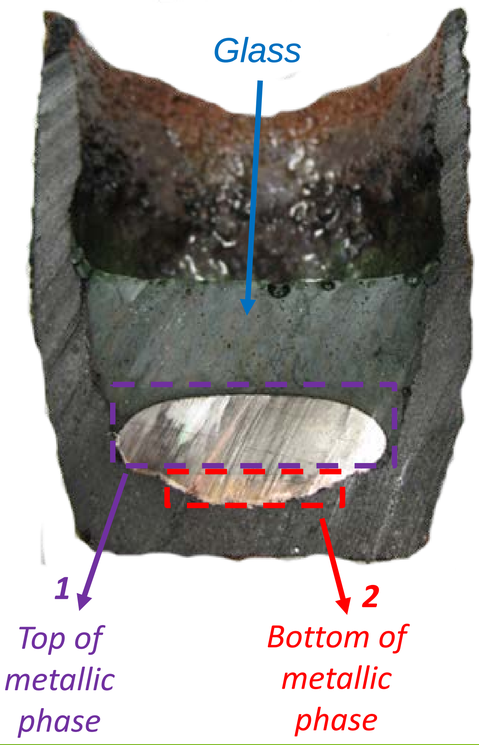


The **technological waste** coming from the production of uranium and plutonium Mixed Oxides fuel (MOx) results **contaminated** by α-emitters and has to be treated as a long-life medium-activity nuclear waste. Treatments are then needed to fix the radio-isotopes in a stable matrix, in order to avoid an accidental release in the environment.

Among the possible solutions, one consists in **melting** such **technological waste** (mainly stainless steel, copper and aluminum scraps) and merging it together **within a SiO_2-Na_2O melt**. A glass containing a complex metallic phase is then produced and will be disposed in a deep geological site.

The presence of numerous elements, the range of temperature and the chemical interactions between the metallic and oxide liquids make this system very complex to describe. The **CALPHAD method** is well suited **to predict** the thermodynamic interactions inside such complex mixtures. Thermodynamic modeling will also provide useful information to optimize the entire process at industrial scale.

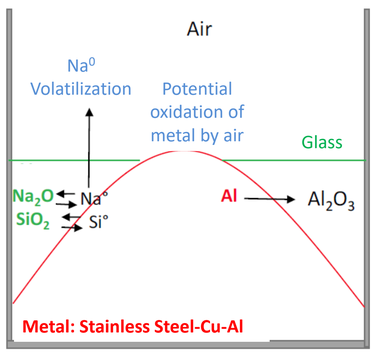
The first step concerns the analysis of the **metallic phase**, here represented as Al-Cu-Fe-Si-U and, especially, focusing on **the behavior of uranium**.



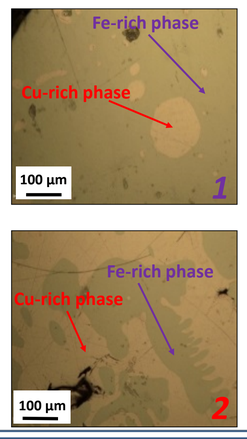
Results

On Pilot Process Scale

Interaction between liquids



- Total oxidation of Al.
- Partial reduction of SiO_2 and Na_2O.
- Total evaporation of reduced Na^0.
- Negligible oxidation due to air.

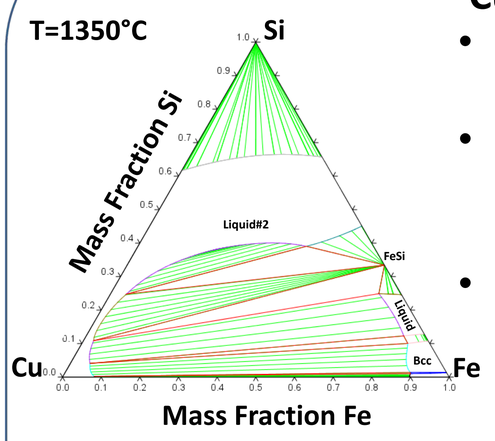


Metallic composition

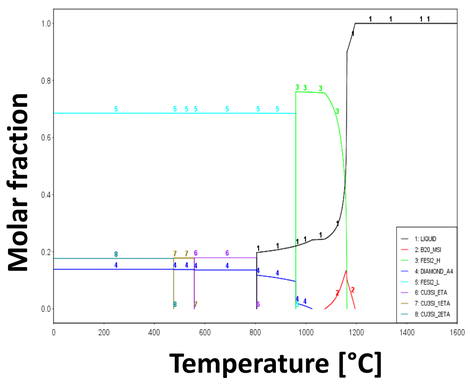
- Top of the metallic side (***1***) mainly made by stainless steel + Si^0, with Cu inclusions.
- Bottom (***2***) the opposite: Cu-rich phase with stainless steel + Si^0 inclusions.
- Almost same composition of phases in both cases.
- Initial Al^0 is not found, while reduced Si^0 is observed in Fe-rich phases.

On Laboratory Scale

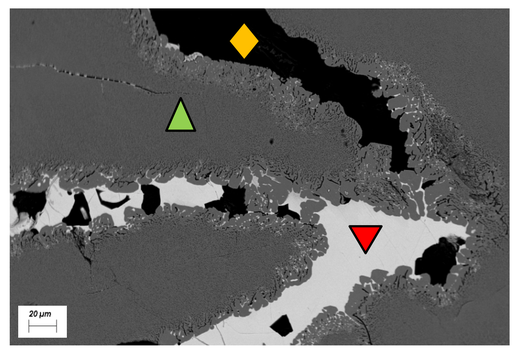
Cu – Fe – Si (Wang, Journal of Phase Equilibria, 2002)



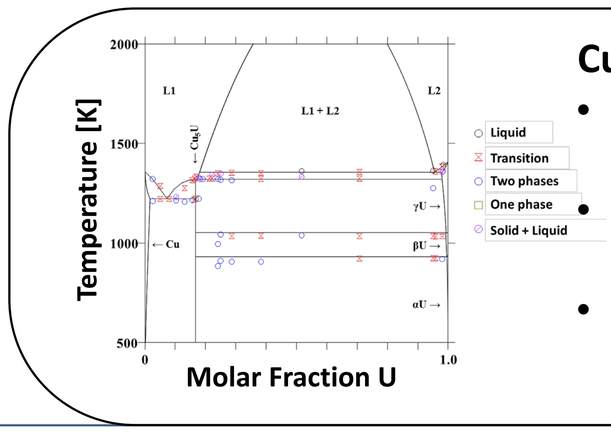
- Above 1170 °C appearance of a miscibility gap in the liquid phase.
- In the Si poor region, both liquids are involved in three phase equilibria with (Fe,Si,Cu)-BCC and FeSi intermetallic.
- At higher temperature, the three phase equilibria disappear in favor of the liquid miscibility gap (see isothermal section at 1350°C).
- Separation of a Cu-rich phase directly from the liquid (see solidification path of $Cu_{22}Fe_{32}Si_{46}$ composition).
- Experimental analyses are in good agreement with the thermodynamic modelling.



- EDS imagine on the sample with composition $Cu_{22}Fe_{32}Si_{46}$ three phases are found, perfectly in agreement with the simulation:
  - Black areas → Diamond
  - Grey areas → $FeSi_2$
  - White areas → Cu_3Si



Cu-U thermodynamic modeling



- Cu-U binary modeled from experimental data
- A large liquid miscibility gap is also present in this system
- The intermetallic phase Cu_5U appears during solidification

Conclusions

This work focuses on some key sub-systems that may form during the treatment of contaminated technological waste:

- **Al is totally oxidized** as result of the reaction with SiO_2-Na_2O, so it may not be considered in the modeling of the metallic phase. On the contrary, **Si is included** as result of the interaction $4\ Al^0 + 3\ SiO_2 \rightarrow 2\ Al_2O_3 + 3\ Si^0$;
- The metallic phase consists of two composition sets, one rich in Fe, the other one rich in Cu. This behavior is strongly related to the presence of a **large miscibility gap** in liquids and (Cu,Fe)-FCC that extents into the Cu-Fe-Si system at temperatures of the vitrification process;
- The Cu – U system is modeled, showing the presence of another miscibility gap. This can suggest that in the quaternary Cu-Fe-Si-U system, U may be mainly solubilized in the Fe-rich side or form an intermetallic phase with Fe.

Perspectives

Next steps:

- Experimental thermodynamic investigation of the other metallic ternary systems: Cu-Si-U and Fe-Si-U;
- Development of a database including the oxide phases of the system;

Future developments:

- Experimental study of the liquid thermo-physical properties (density, viscosity, surface tension) as function of temperature and composition;
- Calculation of the the oxidic/metallic liquids and the crucible interactions