Transient model of a fluorine electrolysis cell.  

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Introduction: In the nuclear fuel cycle, fluorine is produced by the electrolysis of the molten salt KF-2HF. It is a complex process to study since hydrofluoric acid and fluorine are hazardous and highly corrosive. A 3D-model of a lab-scale fluorine electrolysis cell has been developed to increase our understanding of this process, using the electric currents and the bubbly flow interfaces to simulate the flow resulting from the production of gaseous hydrogen and fluorine, and using the heat transfer and the transport of concentrated species interfaces, to model the heat transfer inside the cell and the consumption of the species at the electrode.

The model and the geometry: Half of a lab-scale electrolysis cell was considered because of a reflection symmetry.

![Figure 1. Principle of the process simulated (left) and the mesh used in this model (right).](image1)

At the interfaces between the two electrodes and the electrolyte, gas bubbles are generated and chemical species are consumed. Water is flowing in the small heat exchanger located behind the cathode.

One major feature of this model is to take into account the solidification of the electrolyte that occurs when the temperature and/or the HF concentration drops. The apparent heat capacity method has been used to take into account this phenomenon.

1. Validation of the apparent heat capacity method to model the solidification:

A reactor filled with KF-2HF at 95 °C was cooled down to 40 °C and the temperature was measured during the whole experiment at different points. A COMSOL model was built and the simulated temperature curves were compared to the measured temperature curves.

![Figure 3. Comparison between simulated and experimental temperature curves for solidification.](image3)

2. Evaluation of the thermal conductivity of solid KF-2HF:

The same reactor as before, filled with solid KF-2HF, was heated from 30 °C to 55 °C. Simulations were performed for several values of the thermal conductivity and the simulated results were compared to the experimental results. 3 experiments were realised and the thermal conductivity of solid KF-2HF was assessed.

![Figure 4. Comparison between simulated and experimental temperature curves.](image4)

3. Results:

We have calculated the temperature and the voltage for two currents (170 mA and 430 mA) that were applied to the cell.

![Figure 6. Temperature inside the cell after 200s at I = 170 mA.](image6)

![Figure 7. Solidification of the electrolyte around the heat exchanger after 200s at I=430 mA (1: all solid ; 2: all liquid).](image7)

The impact of the solidification of the electrolyte on the cathode was illustrated thanks to this model. For a high current density at the cathode, the HF concentration drops under a critical value. Since the solidification temperature is highly dependent on the HF concentration, an insulating solid phase begins to form on the cathodic surface which triggers an increase of the anodic potential.

![Figure 8. Zoom on the solidification of the electrolyte on the cathode at I = 430 mA after 200s.](image8)

4. Conclusion: We have built a 3D-model with new thermodynamic data for the KF-2HF electrolyte. With this model, we observe solidification processes at the cathode. This will be compared to experimental data.