

Title for the AIChE conference abstract

Inhibiting corrosion in molten fluoride salts: investigation on Flinak

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Hydrogen is hailed as the non-polluting energy carrier of the future. Three techniques are currently investigated to produce it in industrial quantities: steam reforming of methane, high-temperature electrolysis of water and catalyzed decomposition of water by thermochemical cycles. The latter two will be free of carbon emissions, provided that the primary energy source is so: they both require a high-temperature heat supply. This carbon-free heat could be provided by a high temperature nuclear reactor.

The current design for this reactor is a high-temperature helium-cooled reactor, to be built by 2017 as part of the New Generation Nuclear Plant (NGNP) program. It would be linked to a power-conversion unit producing electricity, and an intermediate heat exchanger loop connected to the hydrogen production plant.

Two candidate heat conveying fluids are under consideration: molten fluoride salts and pressurized helium. Molten fluoride salts are very stable on a wide range of temperatures. They have low vapor pressures and therefore do not need to be highly pressurized to avoid two phase flows. Their fluid mechanics properties in the range of temperatures considered (500°C to 1000°C) are similar to those of room-temperature water, as well as their optical properties (their transparency to visible light will make in service inspections much easier than in the case of liquid metals). They have very good heat transport qualities, and have only benign and non-corrosive interactions with dry air and CO₂. They therefore appear to be prime candidates for the application considered, were it not for the corrosion issues associated with their use at high temperatures.

The choice of the salt's components is dictated by their compatibility with the structural alloy components, which should not be able to reduce the salts to their metal form (NaF to Na, KF to K for example). Operation of the Aircraft Reactor Experiment (ARE) in the 50s and the Molten Salt Reactor Experiment (MSRE) in the 60s have demonstrated the compatibility of a fluoride fuel mixture with Ni-based container alloys at maximum operating temperatures of 710°C. The studies then performed by ORNL concluded that the corrosion, which consisted of the formation of soluble alloying fluorides in the hot part of the loop and their ensuing deposition in the cold part, could be reduced to

acceptable levels by keeping the redox potential of the solution low, and the salt clear of ingress impurities such as moisture or oxygen.

This return of experience is promising enough that fluoride salts shall be considered a viable alternative to pressurized helium if reducing conditions can be maintained in the salt's loop. Differences between the MSRE and the NGNP's intermediate heat loop need however to be accounted for:

1. the salts to be considered will be deprived of the very reducing uranium and thorium ;
2. beryllium, used in the MSRE as a reducer, is a toxic metal and shall not be used ;
3. the higher operating temperatures one would wish to operate these systems at result in aggravated corrosion rates.

Novel approaches are thus required to ensure a safe and durable operation of this system.

Three methods exist to control the redox state of molten fluoride mixtures, which can be evaluated by the value of the 'fluorine potential', defined by $\Delta F_2 = RT \ln p(F_2)$. The lower the potential, the more reducing will be considered the environment, and the less extensive will be the corrosion. They are:

- gas-phase control: fixing the F_2 partial pressure by $\frac{1}{2} H_{2(g)} + \frac{1}{2} F_2 \rightarrow HF_{(g)}$
- major-metal control: example in Flibe $Be(s) + F_2 \rightarrow BeF_2(solution)$
- dissolved salt control by use of a divalent fluoride $CeF_3(sol) + \frac{1}{2} F_2 \rightarrow CeF_4(sol)$

The eutectic Flinak (46.5 LiF, 42 KF, 11.5 NaF in mol%) was chosen for our study. In the situation at hand, two problems shall be considered:

1. mitigation of the structural alloys' corrosion during normal operations,
2. mitigation of the accidental ingress of the very corrosive mixture of SO_2 and concentrated H_2SO_4 used in the proposed hydrogen production process.

The protecting system to be designed, can be thought of in the following terms:

1. 'ubiquitous' or 'local'
2. permanent, or punctual.

The ideal solution would be ubiquitous (control of the redox state is provided throughout the loop) and permanent (in opposition to a punctual 'emergency-type' system, whose maintenance and switch-on mechanism might prove problematic. An emergency system would indeed require a trigger detecting the change in oxidized species).

An ubiquitous and permanent system could be obtained by dissolving in the salt a buffer species that would capture the oxidizing species. An online processing of the heat conveying fluid would be required to strip the salt of the neutralized buffer, and inject a fresh supply of buffer. The engineering involved in this process will be hard to design, given the requirements that would need to be set on the chemistry control side of operations.

An intermediate solution would be to allow for the buffer to be punctually regenerated. The system could be then described as ubiquitous and semi-permanent. An example of how this could work is provided by the MSRE, where the redox control was provided by the uranium in solution: depending on the redox potential of the salt, the uranium would switch from U^{3+} to U^{4+} and the container walls still be protected since their alloys were more noble than uranium. The fluorine potential would then be fixed by the ratio of the activities of UF_4 to UF_3 . To change the value of this ratio and regenerate U^{3+} from U^{4+} , a rod of beryllium was momentarily (for a few hours) dipped into the salt: $2UF_4 + Be \rightarrow 2UF_3 + BeF_2$.

This system can partly explain the very low levels of corrosion that were reported for the MSRE reactor and tubing.

In the case of Flinak, none of the salt's components has this inherent buffer capacity, which will only be obtained via the multiplicity of valence states. Yet, dissolving such species as lanthanide fluorides in the salt would work in a similar way, as has been proposed by the ORNL team of D. Williams et al.

Our approach has been to look for an oxygen getter that would prevent the ingress oxygen and moisture from attacking the walls, capture it and deliver it to a cleaning trap where it would be regenerated. Means to control the fluorine potential would be provided by a metal-control method. Our proposal is to associate the dissolution of an aluminum fluoride with a local contact of the salt with a liquid sodium bath, and a particle filter (via a cold trap if needed). The aluminum fluoride would capture the ingress oxygen, and convey it to the filter in the form of alumina (very stable oxide and insoluble in Flinak – as pointed out by Brooker, Berg, von Barner and Bjerrum in '*matrix isolated Al₂O₆(2-) ion in molten and solid LiF/NaF/KF*'). In doing so, fluorine ions would be discharged in the salt, and then captured in the sodium bath to be converted to sodium fluoride. The liquid sodium would act as a potential fluorine fixer. Although sodium is a very reactive metal, extensive experience has been gathered regarding its use in industrial systems, and how to prevent it from reacting with oxidizing contaminants and catching fire.

Issues that need to be investigated in doing so are:

1. Is this effective in setting a low fluorine potential in the system?
2. What form does the ingress oxygen take? Alumina as expected, or sodium oxide? Alumina would be gotten rid of via filtration, and the sodium oxide could be cleaned via cold-trapping as is done in liquid metal cooled reactors such as Phenix.
3. Does the salt composition change when it goes through the liquid metal bed? If so, does this impact the heat exchanging properties of the fluid?
4. Is the liquid metal Na soluble in the salt at the redox state Na^0 ?

A thermodynamic evaluation was performed to assess the extent to which these reactions would take place. However, those evaluations can hardly be trusted when the activity coefficients of the different species in solution (as diverse as Na^0 , $Na_3AlF_6(l)$, NaF ,

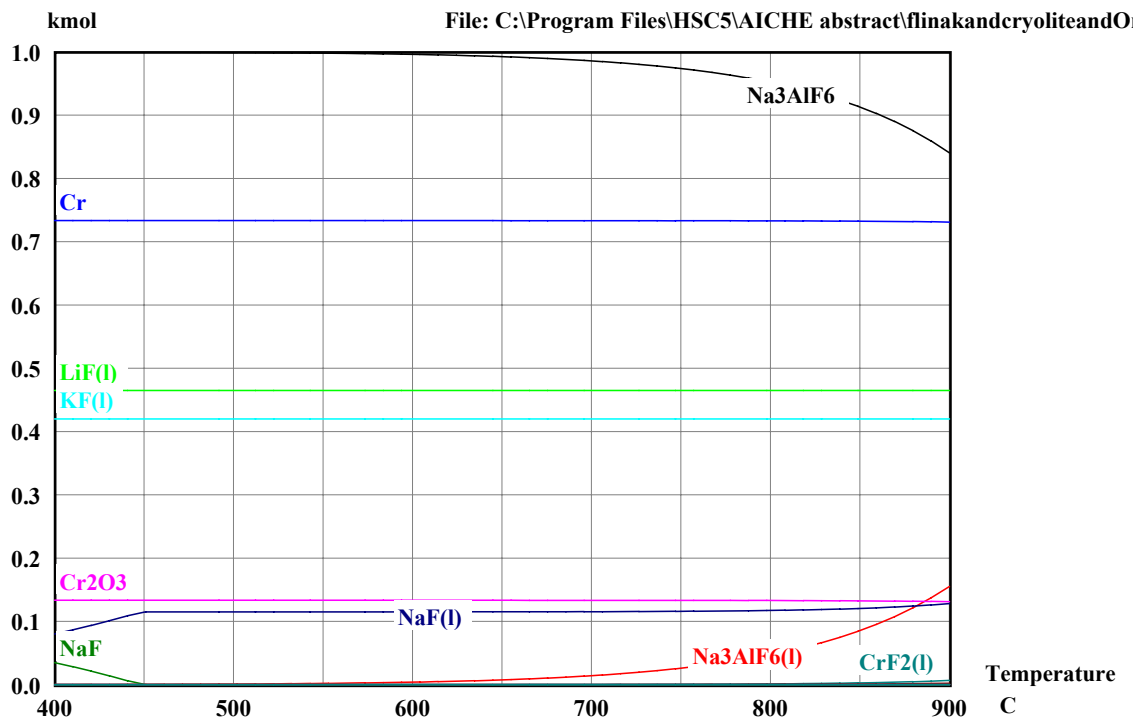
Na₂O ...) are not known. However they showed that the thermodynamics for the expected reduction of ingress oxygen (here: 0.2 moles of O₂ in solution) is 0.2 moles for both figures below? work perfectly well towards the formation of Al₂O₃, and the protection of the chromium in the structural alloys (which is the least stable of the alloying elements with respect to attack by fluorine and/or oxygen, when activity coefficients are all deemed equal to 1 in the alloy).

Common initial states: 1 kmol of Cr, 1 kmol of liquid Flinak, 1 kmol of Na₃AlF₆ (cryolite).

Cryolite is initially present, but not Na(liquid):

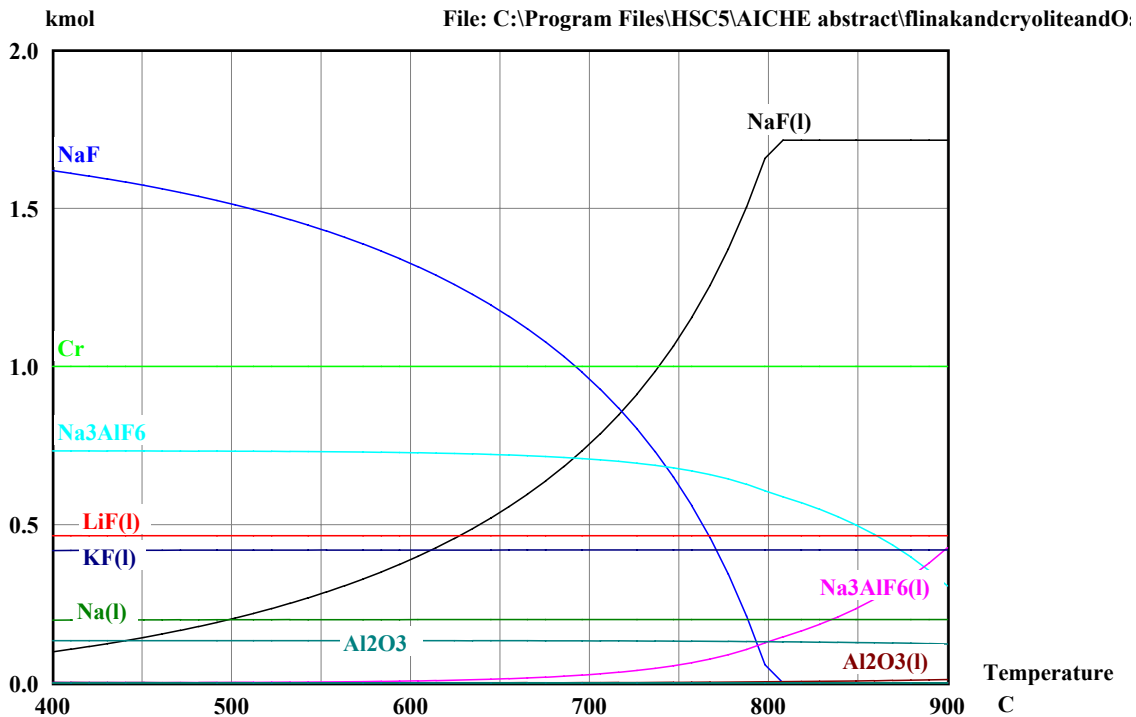
Oxidation of Cr into CrF₂ and Cr₂O₃. Cryolite goes into solution as the temperature rises. The salt composition is not altered.

It would be helpful to label the figures as figure 1 ... and refer to them in the text



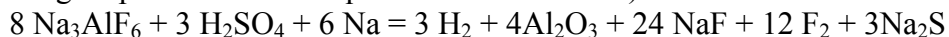
Cryolite and Na(liquid, 1 kmol) are initially present:

Cr is protected, and Al₂O₃ is formed (and no Na₂O is): the corrosion issue is dealt with. Significant alteration of the salt's composition occurs (formation of NaF and NaF(l)).



The previous calculations are only indications. They lack exactitude in the fact that the activity coefficients were all assumed equal to one – which is most likely false in such an ionic liquid. Moreover, the calculations were made assuming that all the species would be present at the same time at the same place, and that for one mole of salt going through the liquid metal bath, it would be in contact with one mole of liquid sodium. However, the most practical way to implement this system would be to dissolve the cryolite in the cold part of the loop, and saturate the salt with it. The concentration of the cryolite would then not exceed the value of its solubility in the cold part (assumed to be at 550°C), which is around 570 ppm (as reported by Brooker, von Barner, Bjerrum et al). The cryolite’s ability to capture oxygen by forming alumina would then be limited by this solubility value.

However, this provides us with an interesting hint to solving corrosion issues in molten salt systems: given that the concentration of dissolved cryolite would be set constant in the salt, small leaks that are implied by the industrial use of a chemical plant would be easily detected (when H₂SO₄ is leaking, H₂ will be generated) and it can be detected in the gas space where the liquid Na bath would be).



Experimental work is in progress to determine the solubility of Na^o in molten flinak at 550°C. Ultimately, this Liquid Salt – Liquid Metal experiment will be used to check the value of the cryolite’s solubility in flinak, and extended to checking how oxygen bubbled into the gas could be captured by the cryolite.

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