## C/SIC HEAT EXCHANGER HEAT TRANSFER AND SAFETY ANALYSIS

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#### ABSTRACT

This report is composed of two parts. The first part summarizes the thermal design of compact offset fin ceramic plate heat exchangers. The unit cell and header structures are described in detail. The heat transfer and pressure loss calculation correlations are summarized. The thermal design procedures are given in details. The second part summarizes the survey and investigation of corrosion control methods in liquid fluoride salts to meet the safety requirement for liquid salt as an intermediate fluid between nuclear loop and hydrogen production loops. Specific focus is set on the KF-LiF-NaF eutectic (Flinak), one candidate salt for the NGNP intermediate loop. After summarizing some of the lessons learned from the Molten Salt Reactor Experiment (MSRE) which ran from 1965 to 1969, the requirements set by the NGNP are detailed. The Fluorine potential is defined as the main variable to describe the chemistry of this system. The thermodynamics of the corrosion process is explained. Ideas to mitigate oxygen and sulfur ingress in the loop are discussed. The report also describes what remains to be understood and proposes means to move forward from the present situation to the demonstration of the feasibility of fluoride salt use as heat exchanger fluids for high-temperature applications.

# PART 1 - OFFSET FIN COMPACT PLATE HEAT EXCHANGER THERMAL DESIGN

## 1. UNIT CELL DESCRIPTION

Offset strip fin compact plate heat exchangers [Manglik and Bergles, 1995] have a high degree of surface compactness, and substantial heat transfer enhancement is obtained as a result of the periodic starting and development of laminar boundary layers over uninterrupted channels formed by the fins and their dissipation in the fin wakes. There is an associated increase in pressure drop due to increased friction and a form-drag contribution from the finite thickness of the fins. Typically, many offset strip fins are arrayed in the flow direction, as schematically shown in Fig. 1. Their surface geometry is described by the fin length l, height h, transverse spacing s, and thickness t. The fin offset is usually uniform and equal to a half-fin spacing.



Figure 1: Geometrical description of a typical offset strip fin core (Manglik and Bergles, 1995).

A recent high temperature heat exchanger study for nuclear hydrogen production (Peterson, et al., 2003) has suggested that carbon-coated composite materials such as liquid silicon infiltrated (LSI) and polymer infiltrated (PI) chopped fiber carbon-carbon preformed material potentially could be used to fabricate high-temperature plate fin heat exchangers. To fabricate compact plate-type heat exchangers, one side of each plate is die-embossed or milled, to provide appropriate flow channels, leaving behind fins or ribs that would provide enhanced heat transfer, as well as the mechanical connection to the smooth side of the next plate. For green carbon-carbon material, milling can be performed readily with standard numerically controlled milling machines. Alternatively, plates can be molded with flow channels, as has been demonstrated for carbon-carbon composite plates fabricated at ORNL for fuel cells and more recently in preliminary molding tests for PIP material by COI. For assembly, the ends of the fins and other remaining unmachined surfaces around the machined flow channels would be coated with phenolic or polymer adhesive, the plate stack assembled, header pipes bonded and reinforced, and the resulting monolith pyrolysed under compression. Then liquid silicon would be infiltrated to reaction bond the plates and headers together, or multiple stages of polymer infiltration and pyrolysis would be performed, forming a compact heat exchanger monolith.

Figure 2 illustrates a discontinuous fin geometry for liquid salt-to-helium compact heat exchangers. The cross-sectional area of the fins and the thickness of the remaining plate below the machined channels can be adjusted to provide sufficient strength to resist thermal and mechanical stresses. For the salt-to-helium heat exchangers in the intermediate loop, mechanical stresses are relative large. For the case in which the heat exchanger is immersed into a helium environment, detailed stress analysis has indicated that the stresses are dominantly compressive and can be accommodated with relative ease. The spacing between rows of fins,  $P_y - I$ , should be sufficiently large to allow the flow to pass between rows without accelerating in the constriction between the ends of fins, as shown in Figure 3. Conversely, it is desirable to minimize this distance to minimize stress concentrations at the ends of the fins. The optimal fin length is then around



**Figure 2**: Cut away view through a plate showing alternating liquid salt (top and bottom arrows) and helium (middle arrows) flow channels. Dark bands at the top of each fin indicate the location of reaction-bonded joints between each plate.



Figure 3: Dimensions showing minimum staggering of flow fins,  $P_y$  - l, required to maintain full flow area to minimize pressure loss.

## 2. HEAT TRANSFER AND PRESSURE LOSS CORRELATIONS

To better understand the physical phenomena and enhancement mechanisms in offset strip fin heat exchangers, Manglik and Bergles (1995) reanalyzed existing empirical f (average Fanning friction factor) and j (Colburn factor = St  $Pr^{2/3}$  or Nu/(Re  $Pr^{1/3}$ )) data for the actual compact heat exchanger cores. The asymptotic behavior of the data in the deep laminar and fully turbulent flow regimes was identified. The respective asymptotes for f and j were shown to be correlated by power law expressions in terms of Re and the dimensionless geometric parameters  $\alpha$ ,  $\delta$ , and  $\gamma$  which are defined in Figure 1. Finally, rational design equations for f and j were presented in the form of single continuous expressions covering the laminar, transition, and turbulent flow regimes:

$$f = 9.6243 \operatorname{Re}^{-0.7422} \alpha^{-0.1856} \delta^{0.3053} \gamma^{-0.2659} \cdot \left(1 + 7.669 \times 10^{-8} \operatorname{Re}^{4.429} \alpha^{0.920} \delta^{3.767} \gamma^{0.236}\right)^{0.1}$$
(2)

$$j = 0.6522 \operatorname{Re}^{-0.5403} \alpha^{-0.1541} \delta^{0.1499} \gamma^{-0.0678} \cdot \left(1 + 5.269 \times 10^{-5} \operatorname{Re}^{1.340} \alpha^{0.504} \delta^{0.456} \gamma^{-1.055}\right)^{0.1}$$
(3)

These equations correlate the air experimental data within  $\pm 20\%$ . The experimental data ranges are:  $120 \le \text{Re} \le 10^4$ ,  $0.134 \le \alpha \le 1.034$ ,  $0.012 \le \delta \le 0.006$ ,  $0.038 \le \gamma \le 0.195$ . Equation (3) is applicable over a moderate range of Prandtl numbers, from 0.5 to 15. The hydraulic diameter is defined as

$$D_{h} = \frac{4A_{c}}{A/l} = \frac{4 \cdot s \cdot h \cdot l}{2(s \cdot l + h \cdot l + t \cdot h) + t \cdot s}$$

$$\tag{4}$$

Joshi and Webb (1987) gave a correlation to calculate the limit on the laminar flow range:

$$\operatorname{Re}^{*} = 257 \left(\frac{l}{s}\right)^{1.23} \left(\frac{t}{l}\right)^{0.58} D_{h} \left[t + 1.328 \left(\frac{\operatorname{Re}}{l \cdot D_{h}}\right)^{-0.5}\right]^{-1}$$
(5)

For the ceramic heat exchanger shown in Figure 2, fins are not rectangular shape but half circular which can significantly reduce pressure loss while not affect heat transfer enhancement. So a reduced fin thickness can be used in equation (2) and (3) to reflect round front fin effect. An effective fin thickness coefficient  $C_{\text{fin}}$  is used to calculate  $\delta$  and  $\gamma$ :

$$\delta = \frac{C_{fin} \cdot t}{l} \tag{6}$$

$$\gamma = \frac{C_{fin} \cdot t}{s} \tag{7}$$

Where  $C_{fin} = 0.5$ . Nu number is calculated by

$$Nu = j \cdot \text{Re} \cdot \text{Pr}^{1/3} \tag{8}$$

#### **3. DESIGN PROCEDURES**

#### **Counterflow Heat Transfer Region**

The goal of designing a heat exchanger is to specify heat exchanger dimensions and inlet/outlet manifolds, given hot and cold fluids inlet/outlet temperatures, one fluid mass flow rate or total heat transfer capacity (power). This section will summarize the procedures to calculate counterflow heat transfer region; next section will discuss the design of inlet and outlet manifolds. For plate heat exchanger, the frontal area can be selected as a variable design parameter, which is constrained by the heat exchanger layout design in a high pressure vessel and by reasonable pressure losses. The heat exchangers will be immerged in high pressure fluid so a high pressure vessel is necessary.

A relation commonly used in heat exchanger design is

$$q = UAF_G \Delta T_{\log-mean} \tag{9}$$

where the log mean temperature deference (LMTD) is defined by

$$\Delta T_{\text{log}-mean} = \frac{(T_{h,out} - T_{c,in}) - (T_{h,in} - T_{c,out})}{\ln[(T_{h,out} - T_{c,in})/(T_{h,in} - T_{c,out})]}$$
(10)

LMTD is the average temperature difference calculated for the case of true counterflow. If the heat exchanger is a counterflow unit, the nondimensional factor  $F_G$  is unity; for all other flow arrangements,

 $F_G$  is less than unity and has been calculated for a variety of flow configurations and is presented in graphical form [Kays & London, 1984]. For plate type heat exchangers, it is desirable to maximize the fraction of the total flow area that is counterflow, rather than crossflow, and to maximize the uniformity of the flow distribution across the heat exchanger surface area, to bring  $F_G$  closer to unity. The overall thermal conductance U is calculated by

$$\frac{1}{UA_w} = \frac{1}{(A_h/A_w)\eta_{0,h}h_h} + \frac{t_w}{k} + \frac{1}{(A_c/A_w)\eta_{0,c}h_c}$$
(11)

 $\eta_0$  is overall surface effectiveness and calculated by the following equation:

$$\eta_0 = \frac{A_w + \eta_f A_f}{A_t} \tag{12}$$

where

$$\eta_f = \frac{\tanh(ml)}{ml} \tag{13}$$

$$m = \sqrt{\frac{2h}{k\delta}} \tag{14}$$

If the heat exchanger capacity and inlet and outlet temperatures for the hot side are given, the hot side mass flow rate  $\dot{m}_h$  can be calculated by,

$$\dot{m}_{h} = \frac{q}{c_{p} \cdot \left(T_{h,in} - T_{h,out}\right)} \tag{15}$$

Figure 4 shows the main procedures to design the heat exchanger core regions. The pressure losses are calculated by:

$$\Delta p = \frac{4f \cdot L \cdot \rho \cdot u^2}{2D_h} \tag{16}$$

where L is total flow length in the core heat transfer region, u the fluid speed. The goal of the core region design is to obtain the total heat transfer area needed, frontal area, flow length, and pressure losses information. The cross-section shape is decided by the header design and the way to arrange heat exchanger modules in vessel.



Figure 4: Core heat transfer region design procedures.

## **Inlet/Outlet Manifold Designs**

For the applications where there is a substantial difference between the volumetric flow rates of the two fluids, we can follow these criteria to design an optimal ceramic plate heat exchanger for counterflow heat exchange. The design criteria are:

- **High volumetric flow (HVF) fluid**: Maximize the HX frontal area, and minimize the flow area variation through the heat exchanger, to minimize pumping power. The heat exchanger is assumed to be immersed in environment containing the HVF fluid, so that the HVF fluid can be pumped through the HX in a manner similar to how air is pumped through a car radiator.
- Low volumetric flow (LVF) fluid: Because the LVF may be a liquid, and the LVF may flow horizontally through the HX, LVF flow paths are horizontal, or slope upward, so that gas bubbles can be reliably purged and the liquid can be reliably drained.

The distribution manifold must provide uniform mass flows to the finned region of the plate, to provide for high effectiveness. Fins are preferred due to their ability to enhance heat transfer, but the finned region of the plate may be subdivided into a number of parallel flow regions, to reduce cross-flow in the finned region. The distribution manifold must do this with a reasonable pressure drop, to avoid excessively high LVF fluid pressures and pumping power (although pumping power will likely be dominated by the HVF).

Cross-flow reduces the overall effectiveness of the HX. Because regions with cross-flow operate with larger temperature differences than counterflow regions, they reduce the temperature difference

available in the counterflow region. Thus it is important to minimize the fraction of the total plate area that operates with cross-flow, which means minimizing the area of the plate occupied by the distribution flow channels.

The HX must be able to sustain transient thermal stresses that would occur if there were a sudden change in the inlet temperature of the LVF or HVF fluid. In general, this is best accomplished by avoiding thick plate regions, which means that the distribution flow channels should be separated by similar spacing as the widths of the fins. Special design attention must be paid to the manifold holes through the plates, where the plate material must be significantly thicker.

Figure 5 shows a preliminary draft plate design for the compact offset fin plate heat exchangers. Helium plates and liquid salt plates are alternatively joined together to form a heat exchanger module. Pressure losses were estimated for the liquid salt side in an actual size heat exchanger module with similar flow distribution structure to that shown in Figure 5. The result shows that flow nonuniformities in both transverse and stack height directions are very small. With average salt speed of 1 m/s in the core heat transfer region and a core heat transfer area of 0.5 m length by 1 m width, the salt speed maldistribution in the width direction is less than 2% of average speed. The pressure losses in inlet and outlet distribution area dominate the total pressure loss. The maximum inlet pipe dynamic pressure is very small relative to the total pressure loss through HX. Therefore, a uniform flow distribution in the height direction will be expected. This type of distribution design has a relative high salt pressure loss. However, due to the small volumetric flow rate of liquid salt, the total pumping power for liquid salt is acceptable and does not affect the net plant efficiency. The helium side plate has several equal spacing flow dividers to reduce flow misdistribution. HX modules in this type of configuration can be arranged side by side to use available space to the maximum content while still can have uniform LVF distribution in HX modules.



Figure 5: Plates design for compact offset fin plate heat exchanger.

## NOMENCLATURE

- A heat transfer area of offset strip fin surface,  $m^2$
- Ac free-flow area,  $m^2$
- D<sub>h</sub> hydraulic diameter, m
- f average Fanning friction factor in the offset strip fin array, dimensionless
- h height of the offset strip fin channel, m
- j Colburn factor [= St  $Pr^{2/3}$  or Nu/(Re·Pr<sup>1/3</sup>)], dimensionless
- k thermal conductivity,  $W/m \cdot K$
- l length of fin, m
- N number of fin channels, dimensionless
- Nu average overall Nusselt number based on hydraulic diameter, dimensionless
- P wetted perimeter, m
- Pr Prandtl number, dimensionless
- Re Reynolds number based on hydraulic diameter, dimensionless
- Re\* transition point Reynolds number, dimensionless
- St Stanton number based on hydraulic diameter, dimensionless
- s lateral fin spacing, m
- T temperature, K
- t fin thickness, m
- U overall thermal conductance,  $W/m^2 \cdot K$

### Greek Symbols

- $\alpha$  aspect ratio *s/h*, dimensionless
- $\gamma$  ratio t/s, dimensionless
- δ ratio t/l, dimensionless
- $\xi$  Darcy friction factor, dimensionless

#### Subscripts

- c cold side
- h hot side
- in inlet
- out outlet
- w wall

## **REFERENCES AND CITATIONS**

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## PART 2 - INVESTIGATING CORROSION CONTROL IN LIQUID FLUORIDE SALTS

#### 1. INTRODUCTION

Interest in fluoride salts has recently revived due to the growing momentum gathered by hightemperature applications of nuclear reactors. Liquid fluoride salts are stable at atmospheric pressure in a broad range of temperatures (~400°C to 1200°C) and are resistant to radiation. They have low vapour pressures and good heat transfer properties. These qualities make them attractive as high temperature reactor coolants or intermediate heat transfer agents. Composed of the most electronegative element, fluorine, and combinations of some very electropositive elements such as lithium, beryllium, sodium, potassium, rubidium, etc., the liquid fluoride salts used as heat transfer fluid are extremely stable compounds. The pure salts do not have the strong corroding power of water, because the products of salt corrosion (metallic fluorides) are less stable than the beryllium and alkali fluorides of the salt, whereas metallic oxides from water corrosion can be very stable. Yet, purity is not a realistic state of operations since contaminants can be introduced in the system via a variety of means including an initially impure salt charge, fluxing of the oxide film that the piping will invariably have, and ingress of impurities such as moisture, air, sulfuric oxide and other hydrogen production fluids involved due to a failure in the salt containment. If no control of corrosion is provided, these impurities can lead to severe attack of the structures in contact with the salt. This process is aggravated by the solubility of the corrosion products in the liquid salt. Solubility being temperaturedependant, the temperature gradient intrinsic to any heat exchanging loop transforms this corrosion equilibrium into a permanent transient: material is continuously dissolved away from the hot part of the loop and deposited in its cold part.

UC Berkeley has studied liquid salts for use as a non-fuel liquid coolant in the Advanced High Temperature Reactor (AHTR) and as a heat transfer fluid for the intermediate heat transfer loop aiming at hydrogen production in the Next Generation Nuclear Plant (NGNP) [Laurenty, et. al., 2005]. One of main issues for the use of liquid salt as intermediate heat transfer fluid is redox potential control to control corrosion rates, and to mitigate any safety related accidents involving ingress of reactive contaminants such as  $H_2SO_4$  or  $H_2O$  that may generate chemically toxic HF. This report descriptes possible approaches to corrosion and redox potential control in fluoride salts. A specific focus is set on the KF-LiF-NaF eutectic (Flinak), one candidate salt for the NGNP intermediate loop. The fluorine potential is used as the main variable to describe the chemistry of this system. The thermodynamics of the corrosion process are explained and experimental methods to investigate some of the unknowns involved in this study are described. Finally, the report describes what remains to be understood and proposes means to move forward from the present situation to the demonstration of the feasibility of fluoride salt use as heat exchanger fluids for high-temperature applications.

## 2. THE CHEMISTRY OF FLUORIDE SALTS

## 2.1 Definition and Control of Redox Conditions in Liquid Fluoride Salts

For liquid fluoride salts, corrosion involves the degradation of a container material due to change in the oxidation state of the container materials. Its impact can be evaluated using thermodynamic equilibria calculations, because the attack of the material at a given temperature will only be favoured if the oxidation products are more stable than the initial species. In the case of the fluoride salts which are the focus of this study (flibe – 2LiF, BeF<sub>2</sub>; flinak – eutectic of KF, NaF, LiF), the initial fluorides are extremely stable compared to the container materials fluorides (see Figs. 1 and 2), and the corrosion level should be low if sufficiently reducing conditions are maintained. In Figs. 1 and 2, the energies of formation of the MF<sub>x</sub> elements mentioned in these figures have been reported per mole of fluorine. This is the most consistent way to compare the relative stability of these elements, with respect to such corrosion reactions as BeF<sub>2</sub> + Cr = Be + CrF<sub>2</sub>.



Figure 1: Energies of formation of relevant fluorides in a typical liquid fluoride salt.



Figure 2: Free energies of formation of relevant fluorides in a Flinak cooled system, in comparison with typical constituents of a liquid fluoride salt.

Despite this great stability of the salt's fluorides in comparison to the structural materials, fluoride salts are known to provide highly corrosive environments under some chemical conditions. This is explained by the potential existence of 'free' fluorine, which will readily attack the containing alloy's components. This effect may be especially severe when impurities are present in the melt (such as oxygen ions). To mitigate this effect, means should be provided to complex the reactive 'free' fluorine. The fluorine potential  $\Delta \overline{G}_{F_2}$  is defined by analogy with the oxygen potential used in metallurgy [Olander, 2002] to quantify this amount of virtually 'available' fluorine. It is not necessary that F<sub>2</sub> be physically present in the system for the metal and its fluoride to exhibit a fluorine pressure, since the reaction of formation of the initial fluorine bearing species can be written as

$$ZF_{n} + \frac{1}{2}F_{2}(g) = ZF_{n+1}$$
(1)

from which we obtain fluorine potential as

$$\Delta \overline{G}_{F_2} = RT \ln p_{F_2} = 2RT \ln (a_{ZF_{n+1}} / a_{ZF_n}) + 2\Delta G^o_{ZF_{n+1}}$$
(2)

where  $p_{F_2}$  is the F<sub>2</sub> partial pressure divided by standard pressure, a solid chemical activity, and  $\Delta G^o_{ZF_{n+1}}$  the standard free energy of formation for  $ZF_{n+1}$ .

That same fluorine potential will determine the extent of metallic corrosion, since:

$$M + \frac{1}{2}F_2 = MF$$
 (3)

and the corrosion equation can be written as (3)=(2)-(1),

$$M + ZF_{n+1} = MF + ZF_n \tag{4}$$

leading to

$$[MF] = a_{MF} / \gamma_{MF} = 1 / \gamma_{MF} \cdot K_{r} \cdot a_{M} \cdot (p_{F_{2}})^{1/2} = 1 / \gamma_{MF} \cdot K_{r} \cdot a_{M} \cdot e^{\Delta G_{F_{2}} / 2RT}$$
(5)

where [MF] is the molar concentration in salt for MF,  $\gamma_{MF}$  the activity coefficient for MF, and K<sub>r</sub> the equilibrium constant for reaction (3). Obviously, mitigating the fluorine-driven corrosion is equivalent to keeping [MF] as low as possible. This amounts to minimizing the fluorine potential  $\Delta \overline{G}_{F_2}$ . Eq. (2) indicates that this can be done by two means:

- Control of the ratio  $a_{ZF_{n+1}} / a_{ZF_n}$  so that it keeps as small as possible;
- Choice of controlling species with very negative standard free energy of formation.

D. Olander [2002] reviewed three methods to reach this goal:

Gas phase control

By purging the salt with a mixture of  $H_2/HF$  whose ratio is monitored and fixes the fluorine potential that the salt acquires by virtue of sufficient exposure to the gas mixture. This method was implemented in the pre-charge preparation and purification of the Flibe salt charged into the MSRE [*Nucl. Appl. Technol*, 1970, 8 (2) (Entire issue)].

• <u>Major metal control</u>

Addition of a reactive metal M, whose fluoride is present in the salt, can be used to control the fluorine potential, since the two elements whose activities are of interest in equation (2), M and MF will be present.

### • Dissolved salt control

Fluoride salts soluble in the fluoride melt (e.g. Flibe or Flinak) with two valence states close in energy can be used to control the fluorine potential. The effectiveness of this approach depends on the ratio of the two valence states' activities – and is therefore hard to assess since the activity coefficients of these solutions are not known. It proved effective in the MSRE, where the couple  $UF_3/UF_4$  controlled the fluorine potential. Dissolution of rare earths such as Cerium (present as  $CeF_3/CeF_4$ ) has been suggested in Flibe. In the MSRE, the major metal control method was to shift the ratio of  $UF_3$  to  $UF_4$  whose modification might have led to precipitation of uranium out of the salt. It was implemented by periodically contacting the salt with a solid beryllium rod.

These three methods can be understood as providing a sink for fluorine when the fluorine potential increases due to the introduction of contaminants or nuclear transmutation of salt constitutents. This helps prevent the salt from attacking excessively container materials.

### 2.2 Corrosion Mechanisms in Liquid Fluoride Salts

In systems where oxygen is responsible for corrosion, one method to control corrosion is to passivate the structural materials, by forming an oxide layer that provides a barrier to oxygen. In fluoride salts containing systems, the products of corrosion are metallic fluorides. They are soluble in the salt: accordingly, passivation is precluded and corrosion depends directly on the thermodynamic driving force of the corrosion reactions [ORNL-TM-328].

Moreover, no equilibrium state can be reached in a flow loop where temperatures vary from one region to another, due to the gradient of solubility which occurs as a consequence of the temperature gradient in the loop. Container material fluorides are dissolved in the hot part of the loop, and precipitated in the cold part. Since the solubility limits and reaction extent vary from one compound to the other, this process is not uniform: the corrosion susceptibility of alloying additions increased in the order Fe, Nb, V, Cr, W, Ti and Al as shown in tests performed in thermal convection loops operated between 815°C and 650°C with 'Salt 107', i.e. NaF-LiF-KF-UF<sub>4</sub> (11.2, 45.3, 41.0, 2.5 mol%, i.e. flinak with  $UF_4$ , which melts at 490°C). Relatively light attacks of all alloys are reported, except for those containing both Al and Ti or Al and Cr [DEVAN]. Figure 3 shows a comparison of corrosion-product concentrations formed in Salt 107 by various alloving additions as a function of alloy content. This sensitivity to corrosion is confirmed by a NASA study [MISRA and WHITTENBERGER], which states that in the investigated fluoride melts, the tendency for metals to corrode increases in the order: Ni, Co, Fe, Cr, Al. Even though Ti seems 'fragile' with respect to corrosion, adding it to the structural alloys decreases the creep rate and increases the stress rupture life and the ductility of the alloy. This is presumably a result of a reduction in grain boundary shearing and limitation of the growth of cracks by formation of a MC-type carbide [ORNL-4561, 1970]. Moreover, even though Ti is presumed to undergo similar reaction than Cr, it diffuses much less readily than Cr in Hastelloy -N. It was thus concluded that its addition in small concentrations would not prove detrimental [GRIMES, 1970]. The same is likely true for aluminium present in small concentrations.

## 2.3 Salt Cleaning Methods in MSRE

About 1230 kg (2700 lb) of Flibe (<sup>7</sup>LiF – 66%;  $BeF_2 - 34\%$ ) were used in the MSRE, as fuel, coolant and flush salt. These salts were purified prior to being injected in the reactor. The fluorides mixtures were sparged with HF and H<sub>2</sub> to remove oxide<sup>1</sup> and sulfide impurities. They were then sparged with hydrogen alone and contacted with Be metal to reduce residual cationic impurities.

<sup>&</sup>lt;sup>1</sup> The oxides are formed from pyrolysis of the fluoride salts with their absorbed water, when they are heated above their liquidus temperature.

#### 2.3.1 Removal of oxides, sulfides and iodides

So as to avoid corrosion of the MSRE reactor vessel or deposition of solid oxide particles or scales that would hurt the heat transfer, the oxides (soluble to up to 600 ppm in 660°C Flibe [SHAFFER, 1971]) were removed from the salt before its loading, via the reaction

$$O^{2-} + 2HF = 2F^{-} + H_2O(g)$$

This reaction was also used as an analytical tool to determine oxide concentrations at very low levels in the MSRE fluoride mixtures. The ease of oxide removal by hydrofluorination has been reported to increase with decreasing temperature and (as expected given LeChatelier's principle) with increasing partial pressure of HF. The oxide level is reported to have been lowered to 60 ppm +/- 15 ppm [BAES, 1974].



**Figure 3**: Comparison of corrosion-product concentrations formed in Salt 107 by various alloying additions as a function of alloy content [DEVAN].

Sulfur attacks Ni based alloys at high-temperatures. The sulfate's thermal decomposition products (SO<sub>3</sub> and SO<sub>2</sub> or H<sub>2</sub>S) are expected to form metal sulfides and oxides at process temperatures of 600 to 800°C with Ni or Cu. The sulphate ion (SO<sub>4</sub><sup>2-</sup>) can be reduced in a sulphide by hydrogen, and consequently removed as H<sub>2</sub>S when it reacts with HF:

$$2HF(g) + S^{2-} = 2F^{-} + H_2S(g)$$

(7)

(6)

A similar reaction is reported to occur with  $\Gamma$  and could be of similar interest for the NGNP application:

$$HF(g) + I^{-} = F^{-} + HI(g)$$
(8)

 $H_2S$  environmental impact can be efficiently mitigated by capture and neutralization, by industrial processes as developed for coal-burning power plants. As in the case of HF attack on structural metals, control of the  $H_2S/H_2$  ratio should prevent the corrosion of Ni by  $H_2S$ . The sulfates can also be rapidly reduced by active metals. The concurrent reaction  $M^\circ + 2HF = MF_2 + H_2$  must be taken into account to fix a maximum value for HF partial pressure, in order to protect the structural materials [BLOOD, 1964]. The presence of  $H_2$  reduces the corrosiveness of the HF- $H_2O$  effluent mixture, which can be further mitigated by lining the stainless steel containers with pure Cu or Ni. For example, to have 25 ppm NiF<sub>2</sub>, [HF] in H<sub>2</sub> must be 38% by volume at 600°C, and 23% at 500°C.

#### 2.3.2 Removal of metallic impurities

If significant concentrations of structural metal fluorides that are more easily reduced than the chosen salts metals are present in the salt, excessive corrosion of the container is expected to occur by oxidation of the least noble of the alloy additives (e.g., Cr oxidized to  $CrF_2$  in the Hastelloy N<sup>2</sup> used in the MSRE, through such reactions as  $FeF_2 + Cr = Fe + CrF_2$ ). Cr, Ni and Fe fluorides are potentially significant impurities. In the MSRE, they were reduced from solution in the liquid fluoride by a final gas sparge treatment with H<sub>2</sub>:

$$MF_2 + H_2(g) = 2HF(g) + M(s)$$
 in Flibe (9)

While  $CrF_2$  was essentially inert to reduction for practical purposes and  $FeF_2$  hard to reduce,  $NiF_2$  could be removed completely at operating temperature (reaction equilibrium constants for Cr, Fe, and Ni are  $5.5 \cdot 10^{-6}$ , 0.13, and 16000, respectively).

The final phase of the production process involved reducing the remaining potential structural metal impurities, by contacting the mix with an excess of active metal whose cation was present in the salt: Be and Zr (both effective reductants for Cr, Ni and Fe) were proposed and Be was used. Li was not retained due to its ability to reduce the major salt constituent BeF<sub>2</sub>, and its low density, low melting point, and incompatibility with Ni or Cu at the process temperatures. However, the reduction reactions that were to take place with solid reactive metals were kinetically limited. The 'active metals' surfaces became coated by the reduced materials. The effectiveness of the reducing measure was further limited by the efficiency of the liquid/solid separation process. The oxide particles suspended in the melt needed to be filtered. Filtration proved difficult because the suspended oxide particles in the salt mixtures rapidly plugged the sintered nickel filter. Separation of the reduced metal particles thus depended upon decantation. The last encountered problem regarded the need for process control measures: the time saved by the rapid reaction of the strong reducing agents could not be taken advantage of, given that the analytical methods used - chemical analysis -, were time consuming. Finally, this method implied finding a way to add the solid metals to the melt without exposing either to sources of oxide contaminants (air). This procedure would certainly be more efficient if a liquid metal was used instead of a solid one. For flinak, all of the major metals are liquid at temperatures above the melt temperature. Thus contacting of liquid metal with flinak may provide a method for control of fluorine potential.

#### 3. LIQUID SALT AS INTERMEDIATE HEAT TRANSFER FLUID FOR NGNP

In the NGNP, a fraction of the nuclear energy is used for production of hydrogen by a thermochemical and/or high-temperature electrolysis cycle. The chemical plant uses nuclear heat to decompose water into  $H_2$  and  $O_2$ , in a cycle where hot and highly concentrated sulfuric acid and iodine are used as catalysts. Fluoride salts may be considered as heat exchanger agents in the NGNP due to the balance between safety issues and costs – they are less hazardous in terms of chemical reactivity than liquid metals, and much more efficient for heat transfer than helium. The LiF-KF-NaF (respectively 46.5, 42 and 11.5 mol%) eutectic has been emphasized in this study, because of its good thermal properties, its relatively low melting point, and its absence of toxicity (in comparison with Beryllium based salts) except for the potential for the production of HF, a chemically toxic compound, under conditions of ingress of moisture or sulphuric acid.

<sup>&</sup>lt;sup>2</sup> Ni based alloy, 6-8% Cr

The requirement for material compatibility is that the fluorides of the salt constituents should be more stable than fluorides of the containment materials. Thus, alkali metals are the preferred cations for salt constituents and the more noble metals (e.g. Ni) are the preferred container constituents. As explained in part I, along with the thermodynamical formation data, solubility information must be considered in order to assess the salt's potential corrosiveness. This in mind, group IA halide salts (such as Flinak) have a greater solubility for the fluorides of structural materials than the group IIA-halides. Therefore ensuring the salt's initial purity will therefore be even more important for Flinak, a member of the group I A halides.

A first safety feature for NGNP intermediate loop is to separate the nuclear and hydrogen production potential hazard sources. This can be best achieved by spatially separating the two plants. A long distance heat carrier is thus required. Of the two proposed candidates, liquid fluoride salts are in this regard much more attractive than pressurized helium: the pumping power required is much lower and therefore less capital consuming. In addition to the nuclear risk presented by the reactor, the main hazard relative to the operation of the NGNP is the potential for generation and release of toxic chemicals: tritium, HI, HF, I<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, SO<sub>3</sub>, SO<sub>2</sub> and H<sub>2</sub> (when localized) are or could be present in the system, leading to the formation of toxic gas plumes, to contamination of the hydrogen supply or to a possible hydrogen explosion [Forsberg, et. al. 2004]. Two major sources of energy might lead to the rapid dispersal of these chemicals: high pressure gases, rapid heat transfer to volatile fluids (steam explosions), and highly energetic chemical reactions. The use of a liquid as the heat transfer agent makes the first of these three hazards less likely, although the reactor vessel's high pressure boundary in the nuclear island and the pressurized sulphuric acid of the chemical plant are still to be taken into account.

Regarding steam explosions, liquid salt operating temperatures are significantly lower than the temperatures of liquid metals (e.g. aluminium and zirconium) and oxides ("corium" from LWR reactor severe accidents) where energetic steam explosions can occur. Also, liquid salts have high Prandlt numbers that reduce the capability to rapidly transfer heat from the liquid salt to a volatile liquid. During the Aircraft Nuclear Propulsion development program, large scale experiments were done as part of the safety analysis for the program [MANN]. For example, in one experiment 188 kg (414 lb) of flinak (11.5% NaF, 46.5% LiF, 42% KF) at 815 °C (1500°F) was discharged into a 10 ft diameter tank of water at 185°F over a period of 45 seconds. They reported that "Water adjacent to the tank bottom boiled briskly, but not violently enough to shake the steel tank visibly or cause any noise other than the burbling of the boiling water." In a second experiment with 230 kg (505 lbs) of the salt, 2.0 kg of UF<sub>4</sub>, and a capsule of irradiated Na<sub>2</sub>UF<sub>6</sub> to provide a fission product tracer at 815°C, no detectable radioactive material was released from the water pool. The boiling was described as follows. "The physical shock to the water, tank and transfer line was violent during the entire transfer, although the violence was less than explosive. A negligible amount of steam reached the surface of the water, and no entrainment of water or steam into the air was observed." Based upon these observations, risks of steam explosions are likely to be small for the use of liquid salts as heat transfer fluids.

The chemical inertness of the salt results from the very strong attraction between the fluorine and the electronegative metal ions. The reaction  $H_2SO_4$  with NaF-KF-ZrF<sub>4</sub> (10-48-42%) at 1 atm and 850°C is reported endothermic (if completed, gas volume increases by 15%) [Forsberg, et. al. 2004]. Although this reaction should also be assessed with Flinak it is likely that it would have the same or more favourable kinetics and thermodynamics, given that LiF is yet more stable than NaF, ZrF4 and KF.

Tritium can be generated in the nuclear reactor via  ${}^{3}$ He(n, p) ${}^{3}$ H. This reaction accounted for almost all of the He-cooled Fort St Vrain's tritium production. This is a concern if a path exists for the tritium to contaminate the produced hydrogen, headed for commercial use. The diffusion of tritium through the proposed metallic and silicon-carbide heat exchangers, as well as the solubility and diffusion of tritium in the salt must therefore be assessed.

Cost-effectiveness and time constraints prohibit the development of new metallic alloys for the salt containment structures. ASME qualified alloys for high temperatures will therefore be used: it

seems that it would be easier to extend their qualification to liquid salt usage, than to qualify a brand new alloy. Alloy 800H, the only Ni-based alloy qualified for Section III (Nuclear Boilers), contains Al and Ti as anti-creep additives in small concentrations. These are attacked by liquid fluoride salts, although this attack may be small due to their low concentrations. Hastelloy X on the other hand, has been qualified for non-nuclear applications for operations up to 900°C, and contains neither Al nor Ti additives.

Corrosion is a primary design issue affecting the use of liquid salts. In a plant designed to run continuously during 30 years, excessive, continuous leaching of the metals' surfaces is unacceptable. Reducing conditions must be maintained, and in-service monitoring systems will be required. In service monitoring may be simplified compared to that required for opaque liquid-sodium, because the liquid salts are transparent to visible light and are compatible with sapphire windows. In addition to video-surveillance of the conduits, off-normal operations can be detected by gas analysis: in the case of unmitigated moisture or  $H_2SO_4$  ingress,  $H_2$  and maybe some HF will be generated and can be detected. Moreover, corrosion in a fluoride salts system will be kept low if the oxide concentration is reduced. Once again, experience from the operation of liquid metal reactors can be usefully applied to liquid salt systems. A cold trap precipitating dissolved oxides out of the salt can be designed. In typical sodium chemistry control systems, with a series including a 10 micron filter followed by a 60 micron one, the pressure rise on the second filter due to accumulation of NaOH (which precipitated more than NaO), can provide indication of when a filter would need to be replaced.

#### **4. FLUORINE POTENTIAL CONTROL**

Thermodynamic equilibrium modeling tools can be used to assess the extent of reactions between liquid salts, contaminants, and container materials. Up to approximately 5-10 mol%, the solute obeys Henry's Law and the solvent Raoult's law in terms of activity coefficients – i.e. their activity coefficients are constant [BLANDER]. To control fluorine potential, two methods can be used: dissolution of multi-valent fluoride salts and contacting the salt with a reducing metal.

The thermodynamic potential for corrosion can be minimized by maintaining the salt in a reducing condition by using a redox buffer. Electrochemical studies performed at ORNL [CUL, et. al] indicated that suitable redox buffers can be found to minimize corrosion at very high temperatures (Yb or V at concentrations between  $10^{-2}$  and  $10^{-3}$  M). Tables 1 and 2 show some results. The solubility of these rare earths fluorides in liquid flinak needs to be assessed. Studies have been done on CeF<sub>3</sub> [BARTON, et. al., 1970] and other rare earths in flibe during the MSRE as shown in Figure 4, for which they were of interest as fission products. These studies should be repeated on flinak.

| Redox couple    | E° (V) in Flinak at 610°C<br>with Ni/NiF2 ref electrode |
|-----------------|---|
| Yb(III)/Yb(II)  | -1.45   |
| U(IV)/U(III)    | -1.2  |
| V(III)/V(II)    | -0.9  |
| Eu(III)/ Eu(II) | -0.64   |

**Table 1.** E° for several redox couples [CUL, et. al]

|  | Standard reduction potential (V) |                                   |  |  |
|--|----------------------------------|-----------------------------------|--|--|
| Redox couples  | LiCl-KCl at<br>450°C             | 2LiF-BeF <sub>2</sub> at<br>700°C |  |  |
| Li(I) - Li(0)  | -3.62                            | -2.56                             |  |  |
| Mg(II) - Mg(0)                                       | -2.88                            | -                                 |  |  |
| Be(II) - Be(0)                                       | -                                | -1.765                            |  |  |
| Zr(IV) - Zr(0)                                       | -2.13                            | -1.355                            |  |  |
| $\mathrm{Sm}(\mathrm{III})-\mathrm{Sm}(\mathrm{II})$ | -2.035                           | -                                 |  |  |
| Yb(III) – Yb(II)                                     | -1.68                            | -                                 |  |  |
| U(IV) - U(III)                                       | -1.55                            | -1.045                            |  |  |
| V(III) - V(II)                                       | -1.07                            | -                                 |  |  |
| $\mathrm{Eu}(\mathrm{III})-\mathrm{Eu}(\mathrm{II})$ | -0.86                            | -                                 |  |  |
| Reference<br>couples                                 |                                  |                                   |  |  |
| $\mathrm{HF}-^{1\!\!/_2}\mathrm{H}_2$                | -                                | 0                                 |  |  |
| $\frac{1}{2} Cl_2 - Cl^2$                            | 0                                | -                                 |  |  |

 Table 2. Standard reduction potential for several redox couples [BARTON et al.]

In the MSRE, the fluorine control was provided by the dissolved uranium. As long as  $UF_3$  was present in the salt, a reducing and non-corrosive environment was maintained. However,  $UF_3$  was gradually converted to UF<sub>4</sub>. This was due to the fact that the fission products total valence was higher than 3 (slightly less than 4 per fission)<sup>3</sup>. The UF<sub>3</sub> was regenerated by exposing a rod of Be metal to the salt in the fuel pump bowl (in 10 hours of exposure, about 10 grams of Be were dissolved, potentially to form  $BeF_2^4$ . This reduced 2 moles of UF<sub>4</sub> to UF<sub>3</sub>, along with some corrosion products.

A potentially effective option for contacting the salt with a reducing metal to control fluorine potential is liquid alkali baths. If solubility of a reducing metal in the fluoride salt is high enough, a global fluorine potential control is possible. Evidence of high solubility of beryllium in flibe has been obtained in experiments at INL [PETTI]. These experiments have indicated that the solubility of  $Be^{0}$  in Flibe at 530°C is about 0.1 wt% ( $x_{Be} = 0.0036$ )

Experiments to assess the solubility of sodium metal, Na<sup>0</sup>, in flinak, would be valuable to determine the potential to use active metal redox control for clean flinak, as well as experiments to determine the solubility of potential oxygen-getter species such as cryolite under these conditions.

<sup>&</sup>lt;sup>3</sup> if it had been closer to 4, conversion of UF<sub>3</sub> to U could have been feared by  $4UF_3 = 3UF_4 + U$  which takes place above 1000°C. Because metallic U could precipitate, accidental criticality could occur. <sup>4</sup> The recent results obtained by D. Petti and co-workers at INL suggest that Be° might also have substantial

solubility in flibe melts.



Figure 4: Solubilities of CeF3, LaF3 and SmF3 in LiF-BeF2-UF4 (62.8 - 36.4 - 0.8 mole%).

## 5. Oxygen, Iodine and Sulfur Ingress Control

There are different methods to segregate impurities and ingress products out of a liquid salt system. For example, if impurities are volatile, gas effluent stream removal (gas striping: injecting bubbles and centrifugally separate them) can be used; for insoluble particles, filtration can be applied, for example using sintered nickel filter media. For other impurities (non-volatile and soluble), they must first converted to volatile or insoluble forms and then removed from salt by these two methods. When  $H_2/HF$  gas-phase chemistry control is used, sulfides are removed by this reaction:

$$2HF(g) + S^{2-} = 2 F^{-} + H_2 S(g)$$
(10)

with a reaction equilibrium constant K > 104. Iodides are removed by

$$HF(g) + I^{-} = F^{-} + HI(g)$$
with reaction equilibrium constant K  $\approx 600$  [Beas, 1974]. (11)

Dissolved fluoride species with very stable oxides

#### Rare Earths fluorides

The rare earth oxides are not insoluble enough in flibe to offer a method of separation. However, this conclusion might not be true for flinak, given the very different nature of the two salts: flinak is considered to be made of individual ions, whereas flibe is currently modelled as including polymers of

BeF<sub>2</sub>. Niobium is an interesting case given that the Nb<sup>5+</sup> ion forms a stable oxyon NbO<sub>2</sub><sup>+</sup> in liquid fluorides [Ting]. The affinity of oxide to Nb (V) is large in flinak, resulting in an almost quantitative reaction between oxide and niobium [BARNER, et. al., 1991]. This could be used as a means of eliminating the oxides from the melt, provided that an F getter is available to absorb the F<sup>-</sup> released by the dissolution of K<sub>2</sub>NbF<sub>7</sub> that would be introduced in the melt.

#### Al fluorides

In an experiment aimed at studying  $Al_2OF_6^{2-}$  in molten and solid Flinak [BROOKER, et. al.],  $AlF_3$  and  $Na_3AlF_6$  were added to a flinak melt in small amounts (5-11%). To form the ion that was to be studied, oxide had to be added to the salt. While  $Na_2O$  was sufficiently dissolvable to convert most of the  $AlF_6^{3-}$  (major aluminium ion in the melt when no  $Na_2O$  was present) to  $Al_2OF_6^{3-}$ ,  $Al_2O_3$  was found to be essentially insoluble in Flinak melts at 550°C, even after 20 hours of equilibration: 'attempts to dissolve alumina in flinak were not successful - with 10% added  $AlF_3$  or  $Na_3AlF_6$ , there was no indication of any dissolved oxide in the melt, even after 20 hours of equilibration at 550°C'. This observation is also consistent with the fact that sapphire (aluminium oxide) can be used as a window material with liquid fluoride salts with very low corrosion. Moreover, the  $Al_2OF_6^{3-}$  was found to be metastable in solution, and slowly decomposed to produce insoluble alumina:

$$3 AL_2OF_3^{2-} + 6F^- = Al_2O_3 + 4 AlF_6^{3-}$$
(12)

This result is the basis of our interest in dissolving cryolite ( $Na_3AlF_6$ ) in the cold part of the loop, which would capture oxygen ions resulting from an unwanted ingress anywhere in the loop, and precipitate it as insoluble alumina ( $Al_2O_3$ ) that could easily be segregated away from the melt.

Cryolite is a very well known species, extensively used in the aluminium smelting industry as an alumina solvent. Originally cryolite was mined, and now it is synthesized industrially. The Hall-Héroult process for producing aluminium metal dissolves alumina in cryolite at very high temperature and reduces it in a carbon lined electrolytic cell. The anode is a carbon electrode which is oxidized to  $CO_2$ , and the cathode is the denser reduced aluminium, which sinks to the bottom of the cell (aluminum's specific gravity at 1000°C is 2.284, whereas cryolite's is 2.10) [FRARY, 1948]. Frary also mentions the addition of AlF<sub>3</sub> as a means of neutralizing Na<sub>2</sub>O. It is in this context that most references can be found to the interactions between the aluminium ions and oxygen in alkali halide environments. For example, CURTISS, et. al., [1984] studies the interactions between  $O^{2-}$  and Al<sup>3+</sup>. Cryolite is reported to be partially soluble in flinak (around 0.57 mol% at 550°C). In solution, cryolite is assumed [AUGUSTE, et. al., 2003] to dissociate as

$$Na_{3}AIF_{6} = 3 Na^{+} + AIF_{6}^{-3}$$
(13)

In Brooker's experiment studying  $Al_2OF_6^{2-}$  in molten and solid flinak, when the melt is cooled down,  $K_2NaAlF_6$  is formed and not the expected cryolite. It is therefore worthwhile to study if this species is not easier to find, buy and dissolve than cryolite, because it would most likely dissociate in a similar way to form the reagent we are interested in,  $AlF_6^{3+}$ . It would also be interesting to understand whether this intentional addition of  $AlF_6^{3-}$  in the melt reduces the corrosion of the alloying element Al added to structural materials like Alloy 800H in accordance with Lechatelier's principle, the extent of the reaction

$$6 \text{ MF} (l) + Al(s) = M_3 AlF_6 (l) + 3 M(l)$$
(14)

should be diminished.

Because cryolite melts at a high temperature, we can imagine having a bed of solid cryolite in the cold part of the loop, through which the salt would pass and pick up some  $AlF_6^{3^2}$  up to its saturation limit. The ion would circulate through the whole loop and provide a ubiquitous and permanent means to capture oxygen and sustain a low oxygen potential in the circuit.

#### Ti Fluorides

TiF<sub>4</sub> is stable in air, water and does not form oxide species. Yet, TiF<sub>4</sub> is hydroscopic and forms TiF<sub>4</sub>-2H<sub>2</sub>O complexes, with up to 15% defluorination [JORDA, 1997]. The equilibrium concentration of TiO<sub>2</sub> in the MSRE Flibe based fuel was about 40 weight ppm at 600°C [ORNL-4548, 1970, p. 140].

#### Na metal

Abundant information on the chemistry of liquid sodium is available, due to its use in fast reactors. The only sodium oxide to be formed would be  $Na_2O$  (only oxide coexisting with Na).  $Na_2O$  is dissolvable in Flinak [BROOKER, et. al.], but one would need to determine also whether or not it is even more soluble in the liquid sodium bath. Indeed, as the Na/O phase diagram (Fig 5) shows, the solubility of  $Na_2O$  in sodium quickly decreases with decreasing temperature, and is negligible below  $400^{\circ}C$ . The best accepted analytical expression [NODEN] for the solubility of O in liquid Na is

$$Log_{10}[O_{wppm}] = 6.2571 - 2444.5/T(K)$$
(15)

A cold trap such as developed for the Na cooled fast reactors would therefore be very effective in removing the oxides from the Na bed. However, Na may not be an effective oxygen getter compared to typical container materials like Cr, leading to the need for an alternative oxygen getter like Al.



Figure 5: Phase diagram of the Na-O system, H.A. Wriedt, 1987.

#### 6. Discussions and Conclusions

#### Salt Chemical and Corrosion Control for Different Structure Materials

In NGNP intermediate loop, high-temperature alloys and SiC are potential structural materials. Table 3 shows some potential alloys.

| Alloy       | ASME          | Max T  | Composition  |
|-------------|---------------|--------|--|
|             | qualification | °C     |  |
| 800 H/HT    | Section III,  | 980°C  | 30-35 Ni, <u>19-23 Cr</u> , 39.5 min Fe, 0.05-0.1 C, <b>0.15-</b>      |
|             | VIII          |        | <b>0.60 Al, 0.15-0.60 Ti,</b> 0.30 – 1.2 Al+Ti                         |
| Haynes 214  | No            | 1000°C | 75 Ni (as balance), 16 Cr, 4.5 Al, 3 Fe, 0.05 C, 0.01                  |
|             |               |        | Y, max 0.5 Mn, max 0.2 Si, max 0.1 Zr, max 0.01 B                      |
| Haynes 230  | Section I,    | 900°C  | 57 Ni (as balance), <u>22 Cr</u> , 14 W, 2 Mo, max 3 Fe, <i>max</i>    |
|             | VIII          |        | 5 Co, 0.5 Mn , 0.4 Si, <b>0.3 Al</b> , 0.10 C, 0.02 La, max            |
|             |               |        | 0 .015 B   |
| Hastelloy X | Section I,    | 900°C  | 47 Ni (as balance), <u>22 Cr</u> , 18 Fe, 9 Mo, <i>1.5 Co</i> , 0.6 W, |
|             | VIII          |        | 0.10 C, 1 Mn, max 1 Si, max 0.008 B                                    |

**Table 3.** Potential high-temperature alloys for NGNP

The most striking of these alloys' features is their increased content in Cr in comparison to the MSRE's Hastelloy N as shown in Table 4, knowing that Cr was found to be the least stable for the alloying elements in the MSRE. Increased corrosion of these materials can be expected, all the more that apart for Haynes 214 (not qualified), all have decreased fractions of the noble Ni. The only way to determine which of these would be the most useful would be to test them in heat convection loops. Moreover, the Al content could be an issue: according to a NASA report by MISRA and WHITTENBERGER, the equilibrium concentration of  $M_3AlF_6$  in the liquid salts is so high that alloys containing significant amounts of Al are expected to suffer severe corrosion.

Table 4 Hastelloy for MSRE

| 1 ubic + 11usteric | y for MBRE   |                               |
|--------------------|--|-------------------------------|
| Alloy              | Usage  | Composition                   |
| Hastelloy N        | MSRE   | 68 Ni, 17 Mo, 7 Cr, 5 Fe      |
| Hastelloy N        | MSRE   | 68 Ni, 17 Mo, 7 Cr, 5 Fe      |
| modified           |  | Ti added to improve ductility |
| Hastelloy B        | Proposed for ADTT (accelerator driven              | 65 Ni, 28 Mo, minor Fe, Cr,   |
| (N10001)           | transmutation technology), deemed suitable for use | C, Si, Ti, Co, Mn, Al         |
|                    | with LiF-19.5 CaF2 [MISRA and                      |                               |
|                    | WHITTENBERGER]                                     |                               |

Given the apparent insolubility of  $Al_2O_3$  in Flinak, and were it to be proved absolutely insoluble, passivating the piping and heat exchangers with a layer of alumina could prove to be an efficient way of reducing the corrosion. This proposition seems more reasonable that to estimate the corrosion of a few metallic alloys in NaF, LiF and KF. NASA [MISRA and WHITTENBERGER] performed pot experiments in an alumina crucible. This would also have the beneficial side effect of adding additional impedance to the heat conduction through the piping, and thus limit heat losses to the environment. As suggested by Brain Wirth at UC Berkeley, this could be done by using Ni-Al alloys, and selectively oxidize the Al (given that nickel oxides are much less stable than alumina). If this were to be done with current Hastelloys and other Cr-containing alloys, Cr would also be oxidized in this process - and its oxide would be flushed by the initial charge of the salt, which would be problematic. The efficiency of this technique needs to be assessed: is  $Al_2O_3$  indeed absolutely insoluble in flinak (a very plentiful literature has been assembled on the solubility of alumina in cryolite melts, and might inspire such an in-flinak solubility study)? Would the  $Al_2O_3$  form a stable layer at the surface of the alloy? In the case of currently proposed alloys, would the flushing of the unstable oxides create such a porosity that the protecting  $Al_2O_3$  will flake off?

It has been proposed [HAUTENREICH and ENGEL, 1970] that the low corrosion rate observed in the MSRE may have arisen from surface protection by a film of deposited noble-metal fission products (estimated to be 10 Angstrom thick after 30 months of operation, in March 1968). Another idea would be to deposit some of those species on a very thin layer on the structural materials' surface, if this is feasible and not too costly a procedure.

For SiC structural material, one potential issue is corrosion by liquid salt. One of the major ways to etch SiC is using fluoride salts (creation of SiF<sub>4</sub>). However, if a compact carbon layer coating by

CVD or CVI on the SiC surface, the corrosion may be avoided because work with graphite, where liquid salts have negligible corrosion, shows that liquid salts do not wet carbon nor penetrate into small pores in graphite surfaces.

#### Tritium Control

The value of the diffusion coefficient of hydrogen in flinak was found to be an order of magnitude higher than that of fluorine [KATSUTA and FURUKAWA]. Assuming Henry's Law, the solubility of hydrogen was calculated to be about  $6 \cdot 10^{-4}$  mol hydrogen /cc atm at 500°C. This is reported to be a thousand times higher than that of hydrogen in liquid flibe. Transport of tritium in flibe systems has been studied extensively for applications in fusion energy [PETTI]. A proposed explanation for this difference could be that hydrogen in liquid flinak is not thought to dissolve as a hydrogen molecule, whereas it is thought to be the case in liquid flibe. The hygroscopic character of flinak might also have some relation with this high solubility. This behaviour should also be that of tritium – and is excellent news for the NGNP: if flinak was used as an intermediate heat transfer fluid, tritium generated in the reactor would have very little probability of being found in the finally produced H<sub>2</sub>, because it would be trapped in the salt, and eventually captured by degassing of the salt in the salt chemistry control system. This would not be the case if helium were chosen, because tritium would very easily diffuse away from it.

#### Proposed Designs to Clean the Salt

As is apparent from the previous discussion, for heat transfer applications flinak should initially be as clean as feasible. Gas purging may be implemented, as well as contacting the salt with a bath of liquid Na before charging the salt in the loop. A flush salt may also be run in the loop to dissolve residual oxides on metal surfaces and then discarded before the working salt is charged.

A bypass loop for chemistry control, similar to the Chemistry and Volume Control System (CVCS) typically used in pressurized water reactors, may provide a volume-control tank whose inert (N<sub>2</sub>, Ar) cover gas could be analyzed for H<sub>2</sub> and tritium. Additional tanks may also be provided to dump the salt when the chemical plant needs to be isolated from the nuclear island, so that it would not freeze in the piping. These storage tanks would have large thermal inertia which would delay freezing, but would either be provided with continuous heating to keep the salt liquid, or with a punctually operating heater, turned on when the salt would be required to return to the system. Its volume would allow for thermal expansion of the salt upon heating. Part of the salt could also pass through a centrifugal system designed to separate the gas bubbles out of the liquid. Experience from liquid metal fast breeder reactors and from the MSRE where cover gas<sup>5</sup> was analysed in terms of isotopic composition of tracer Xe<sup>6</sup> may beused, with the modification that in the NGNP case, the gases to be measured are H<sub>2</sub> and HT.

Cleaning of the salt in an  $H_2/HF$  fluorinator with salt protected walls may be adequate protection against corrosion (ORNL 4119). The fluorinator walls could be protected by a layer of frozen salt<sup>7</sup>.

Continuously assessing the oxide content of the salt will be useful, and ways to do so exist. The form that oxides take in pure flinak is Na<sub>2</sub>O, although if an oxygen getter is added (such as aluminium) this species would likely bind oxygen and result in the primary dissolved oxygen species, to the small extent that the oxide might be soluble. To measure this Na<sub>2</sub>O oxide content, ORNL researchers [GOLDBERG, et. al., 1960] reacted the salt with KBrF<sub>4</sub> in a Ni cell at 450°C for two hours. The oxide (here represented by Al<sub>2</sub>O<sub>3</sub>) reacts with KBrF<sub>4</sub> according to:  $2Al_2O_3 + 3KBrF_4 = 4AlF_3 + 3KBr + 3O_{23}$  (16)

<sup>&</sup>lt;sup>5</sup> In the MSRE the bowl of the salt pump was used as the surge space for the circulating loop, and dry deoxygenated He at 5 psig blanketed the salt surface in the pump bowl.

<sup>&</sup>lt;sup>6</sup> To check for the presence of failed fuel elements.

<sup>&</sup>lt;sup>7</sup> Salt studies reported in ORNL 4254 and feasibility demonstrated in ORNL 4344; quantitative studies on the protective layer thickness are reported to have been made by Ignatiev et al. [IGNATIEV, 2000]

with traces of  $Br_2$  and BrF. They then measured the created oxygen manometrically. The detection limit for this method is reported as being a few 100 ppm of oxides. An improvement to the ORNL method was proposed in 1998 [EKLUND], and consisted in switching from a manometric measurement to the use of an yttria-stabilized zirconia (YSZ) oxygen pump, whose detection limit is reported as being as low as 12 microg (i.e. 0.75 micromoles). After reaction with KBrF<sub>4</sub>, the O<sub>2</sub> is swept through a stabilized zirconia electrochemical cell, and "pumped" out with an applied potential across the zirconia membrane. This simple and inexpensive technique can be used for routine analysis of samples in the 10 to 250 mg range (depending on the oxide content). Cyclic voltammograms and electrochemical measurements have been proposed for the same application [ITO, 1986; POLYAKOVA, 1997].

#### Conclusions

It is proposed to use cryolite in solution in the liquid flinak to keep oxygen potential low. Al would react with O to form insoluble  $Al_2O_3$  that can be easily removed from salt. Using a liquid bath of Na keeps reducing conditions (fluorine and oxygen potentials) in loop and reacts with S to form insoluble Na<sub>2</sub>S. Based on experiments at INL that have observed substantial solubility of beryllium metal in flibe, similar solubility may be observed for sodium in flinak. If high solubility does exist, dissolved sodium could provide local control of fluorine potential in the loop. The methods need further theoretical and experimental verifications.

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