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SUBJECT: Thermodynamic Stability of Metals and Their Chlorides in the Presence of UCl_3 and $PuCl_3$

A fast breeder has been proposed, to use UCl_3 and $PuCl_3$ dissolved in KCl-NaCl mixture as the core, and to be cooled by a spray of drops of liquid lead. Possible reaction of UCl_3 or $PuCl_3$ with the liquid lead, and also with the container for the fuel salt mixture, is of interest. Compatibility of the container wall with the liquid lead is also of concern; it appears to me that possible harm to the container can be minimized by cooling the container sufficiently to maintain a layer of frozen salt on the container wall. It is obviously desirable that this frozen salt should be low in uranium or plutonium, and it may very well be a fifth chloride (of low solubility in the melt) deliberately added to form this coat. This would require that the walls be cooled, but if a comparatively thick layer of the solid salt is built up, a relatively small amount of heat must be disposed of in this manner.

However, there may be some objections to using a layer of frozen salt to prevent or minimize corrosion, and, even if used, it may occasionally be lost or broken, and hence the metal container should be chosen to resist corrosion. The choice of material should be influenced by the thermodynamics involved in the reactions considered below:

Salt	$-\Delta F_f$ 500°K	$-\Delta F_f$ 1000°K	ΔF of reaction* 500°K	1000°K	- log, K for Reaction 500°K	1000°K
UCl_3	62	53				
$PuCl_3$	67.5	59.5	-5.5	-6.5	-2.40	-1.42
$TaCl_2$	35	27.5	27	25.5	11.80	5.57
$PbCl_2$	34	27	28	26	12.24	5.68
$FeCl_2$	33	27	29	26	12.68	5.68
$NiCl_2$	27	19	35	34	15.30	7.43
$CrCl_2$	40	32.5	22	20.5	9.62	4.48
WCl_2	10.5	4	51.5	49	22.51	10.71
$MoCl_2$	14.5	8	47.5	45	20.76	9.84
$CuCl$	28	22	34	31.	14.9	6.78

*Reaction is for $1/3\ UCl_3 + 1/n\ M \rightarrow 1/3\ U + 1/n\ MCl_n$.

The free energies of formation have been read from the curves in ANL-5750, "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K" by Alvin Glassner.

Since uranium and plutonium are expected to be present in the salt mixture in roughly equal amounts the reaction $1/3\ UCl_3 + 1/3\ Pu \rightarrow 1/3\ U + 1/3\ PuCl_3$ indicates that metallic plutonium should be present at an activity of 10^{-4} to 10^{-7} that of the uranium (depending on temperature) and hence can be neglected. It is for this reason that the reaction of UCl_3 with the potential structural metal is considered, and not that with $PuCl_3$.

The K whose negative logarithm is given is for the activity quotient with activity equal to unity for each substance in the pure state; that for metal M will be very nearly unity, but it will probably be desirable to keep the activity of U very low, perhaps 10^{-9} or 10^{-10}, to prevent damage to the structural metal by alloying with it. From AERE-R3487, "The Thermochemical Properties of Uranium Compounds" Rand and Kubaschewski, one can estimate the free energy of formation of UFe_2 to be about -14.5 kcal, temperature independent within the precision of the estimate. From this, one obtains $UFe_2 \rightarrow 2Fe(a{=}1) + U(a{=}\underline{a})$, $K_{1000} = 10^{-6.34}$, or activity of $U = 10^{-6.34}$. To keep the uranium content of iron down to low levels it appears that $a_u = 10^{-9}$ or 10^{-10} should be satisfactory. We note that for $1/3UCl_3 + 1/2\ Fe \rightarrow 1/2FeCl_2 + 1/3U$, $K_{1000} = 10^{-5.68}$ or for $UCl_3 + 3/2Fe \rightarrow 3/2FeCl_2 + U$, $K_{1000} = 10^{-17}$; for equilibrium, with $a_u = 10^{-10}$,

$$\frac{a^{3/2}_{FeCl_2}}{a_{UCl_3}} = 10^{-7}.$$

The alkali metal chlorides will greatly lower the activity of UCl_3, and also that of $FeCl_2$; it appears plausible that the activity coefficient of $FeCl_2$ to the 3/2 power will be about the same, at least in order of magnitude as the activity coefficient of UCl_3 (to the first power) and hence we expect (mole fraction of $FeCl_2)^{3/2} \simeq 10^{-7}$ x (mole fraction of UCl_3). If iron should be chosen for the container no harm should arise because of the presence of $FeCl_2$ in the melt, and it may be advantageous to add $FeCl_2$ deliberately to it. On the other hand, a trace of moisture in the original fuel at the time of loading would probably lead to uranium oxides and HCl, which may produce enough $FeCl_2$ (by the reaction $2HCl + Fe \rightarrow FeCl_2 + H_2$) to keep the metallic uranium activity to a very low level. It is interesting to note that, within the precision of the available data, K for the reaction with lead is the same as for iron, and we would thus expect about the same concentration of $PbCl_2$ in the melt as of $FeCl_2$.

Of the cheap metals copper is somewhat better than iron from the point of view of corrosion by the salt, but I suspect that it would be more vulnerable than iron to attack by the lead. The K for reaction with copper has been given in terms of production of CuCl, since that is the chloride which is stable in the presence of metallic copper, but the "complexing" tendencies of the chloride mixture may lead to the formation of $CuCl_2$ (in dilute solution) instead. I have not calculated the K for $CuCl_2$, but I am sure that because of our ignorance in regard to the activity coefficients of CuCl and of $CuCl_2$, it would not be profitable.

From the table of K's given above, calculations analogous to those made above for Fe can easily be made for the other metals. From the point of view of corrosion by the salt, chromium is somewhat worse than iron, nickel is better, and tungsten and molybdenum are much better, but it seems that iron is probably good enough, and compatibility with the lead is probably the more important criterion.

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