

# Materials for building the Stable Salt Reactor

Experience in building the Molten Salt Reactor Experiment in the 1960's showed that corrosion of structural metals by molten salts could be a major constraint on designs. Moltex Energy has made two substantial breakthroughs which essentially eliminate corrosion as a concern permitting use of standard nuclear certified steels throughout the reactor.

Corrosion in molten salts differs in a very fundamental way from corrosion in air and water. Steel is intrinsically vulnerable to corrosion by oxygen and water but can be protected from corrosion by formation of a stable protective oxide layer on its surface that keeps the oxygen and water away from the vulnerable metal. Usually this layer is of chromium oxide which is why stainless steels have high chromium content. A large fraction of alloy science has been devoted to understanding and optimising this protective function and today we have steels which will operate successfully in very harsh wet environments.

Unfortunately, this protective mechanism utterly fails when the corrosive liquid is a molten salt. This is because the oxide layers are soluble in the salt, leaving the metal surface "naked" to the molten salt. Much of our hard won learning in designing corrosion resistant metals is therefore meaningless.

Paradoxically, this makes controlling corrosion by molten salts a rather simpler matter. If the molten salt and the metal surface "want" to react together, they will. Preventing corrosion is therefore essentially about adjusting the metal composition and the molten salt composition so they do not "want" to react together.

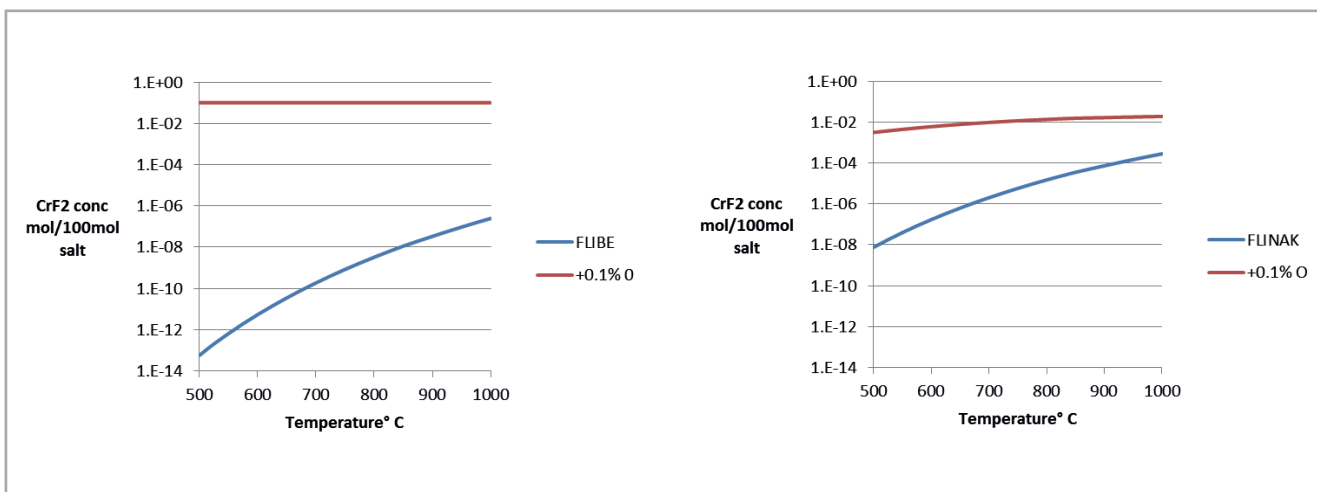
Scientifically, this "wanting" is described by chemical thermodynamics. All chemical systems try to move to their equilibrium point where the chemical energy (the Gibbs Free Energy) of the system is minimised. For iron and water the lowest energy state is iron oxide, which is why steel rusts unless its surface is protected.

For metals in molten salts the corrosion mechanism is for a metal in the alloy, usually chromium, to be oxidised by the salt forming a salt of the metal. If the molten salt is a fluoride salt, then corrosion of steel results in chromium in the steel being converted to chromium fluoride, which dissolves in the molten salt.

For corrosion not to be a problem, the equilibrium, minimum chemical energy, state must be for the chromium to be in the metal form with only tiny amounts of chromium fluoride produced. A good rule of thumb is that if the equilibrium chromium salt concentration is less than 1 part per million (ppm) then corrosion will not be an issue. Modern computation methods allow that concentration to be accurately predicted for any composition of metal and molten salt.

These calculations show that for the molten salts often discussed for use in molten salt reactors (FLIBE and FLINAK) corrosion is indeed a problem.

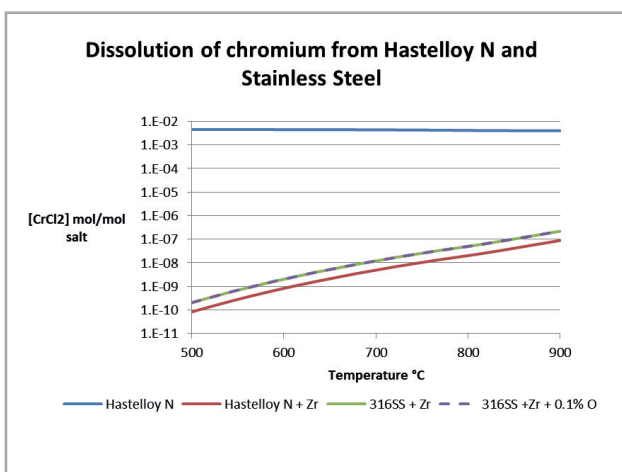
In particular, if even tiny amounts of water or oxygen are allowed into the system then corrosion is inevitable. The graphs below show the equilibrium chromium fluoride concentration for these two salts with and without traces of oxygen. Chromium fluoride levels are as high as 100-100ppm.



In the Stable Salt Reactor, there are two molten salts which could cause corrosion, the fuel salt inside the fuel tubes and the coolant salt outside them. These require different methods to control corrosion.

Fuel salt is chloride based, it contains 40% uranium and plutonium chlorides and 60% sodium chloride. It also contains the full mixture of fission products, almost 1/3<sup>rd</sup> of all elements. Even worse, fission releases some free chlorine as well as the fission products which if not controlled would rapidly react with chromium in the metal to form chromium chloride.

We control this problem in a very simple way by putting small amounts of zirconium metal inside each fuel tube. Zirconium is far more reactive with chlorine than is chromium and it therefore scavenges all the chlorine released. In chemical terms, it renders the fuel salt strongly reducing. The graph below shows the effect of this zirconium addition to the chloride based fuel salt.



The blue line shows how much chromium is dissolved out of the relatively corrosion resistant Hastelloy N if nothing is done to control the released chlorine from fission. The lower curves show the impact of adding zirconium. With either Hastelloy N or standard 316 stainless steel, the concentration of chromium chloride plummets to around 1/1000<sup>th</sup> of a ppm even if oxygen is allowed to contaminate the salt. Corrosion simply cannot occur under those conditions.

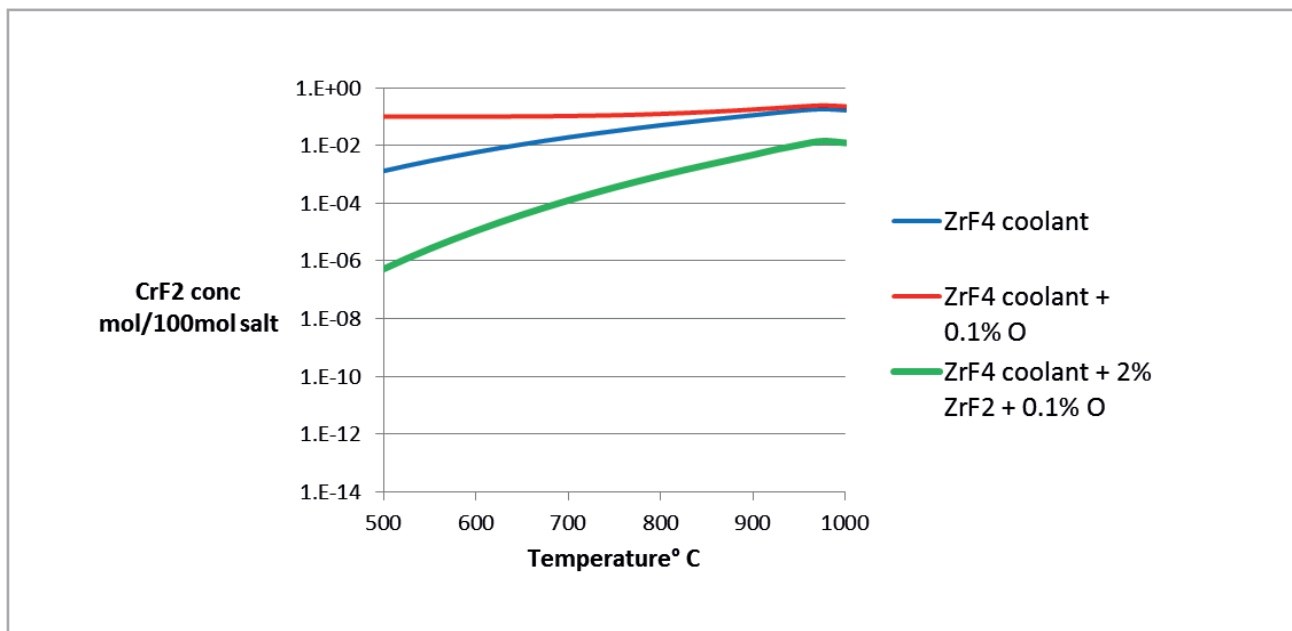
This simple trick of adding zirconium has two additional benefits. One is that it reacts with the fission product tellurium which has been shown otherwise to react with metals making them brittle. The second is that it almost eliminates volatile iodine from the fuel salt which is important since otherwise radioactive iodine will be released from the fuel tubes through their gas vents.

What about the coolant salt? Can the same simple trick be used? Sadly no.

Adding zirconium to the tank containing the coolant salt will indeed prevent corrosion very successfully. Unfortunately however that zirconium will itself migrate around the tank, depositing in dangerous places like in pumps, valves and heat exchangers.

This brings out a key reason for the choice of a coolant salt of 42% ZrF<sub>4</sub>/10%NaF/48%KF. The zirconium salt is normally in the tetravalent

form  $ZrF_4$  but has another stable form, divalent  $ZrF_2$ . Addition of just 2% of the  $ZrF_2$  to the coolant salt transforms its corrosion potential as shown in the graph below.



The protection is not quite as complete as would be achieved with zirconium metal, but it is good enough with chromium fluoride concentrations reduced to around 1/100<sup>th</sup> of a ppm. Since the  $ZrF_2$  is soluble in the coolant salt, there is no problem with deposition of materials in vulnerable parts of the pumped coolant system.

These simple methods to essentially eliminate corrosion make construction of the Stable Salt Reactor with standard stainless steels perfectly practical. This is a huge advantage as nuclear certification of novel molten salt resistant alloys would take many years.

Both methods are however only applicable in the Stable Salt Reactor and not in other molten

salt reactors. The use of “static” fuel salt in tubes makes migration of the zirconium metal used for stabilisation acceptable; there are no moving parts for it to clog. In a system where the fuel salt is pumped, such migration would be unacceptable.

Equally, the use of a coolant salt containing  $ZrF_2$  is only possible in a reactor where no graphite is exposed to the molten salt because the  $ZrF_2$  will react rapidly with graphite forming zirconium carbide. Since most molten salt reactor designs use graphite as a moderator in the reactor core that makes use of  $ZrF_2$  to control corrosion impractical.

The availability of such simple corrosion control systems is therefore still another advantage intrinsic to the Stable Salt Reactor design.