GASEOUS AND VOLATILE FISSION PRODUCT RELEASE FROM MOLTEN SALT NUCLEAR FUEL

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ABSTRACT
Molten salt nuclear fuel can be used in reactors simply by replacing the solid fuel pellets in conventional fuel assemblies with molten salts. One issue with this approach is the fate of gaseous fission products. If the tubes are sealed then the pressure will build up (as happens in metallic fuels). Chemical thermodynamic calculations have been carried out on the nature of the volatile species released and show that, providing fuel salt redox potential is properly controlled, only relatively radiochemically benign isotopes are volatile. Gasses can therefore be simply vented from the fuel tubes into the coolant avoiding pressure increases.

Keywords Molten Salt Gas Vent Nuclear

INTRODUCTION
Nuclear reactors using molten salts of fissile isotopes as fuel continuously produce gaseous and volatile fission products. The major gaseous species are the noble gasses Xenon and Krypton while the most hazardous volatile species is iodine. Molten salt reactors typically sparge their fuel with helium which removes noble metal fission products as foams but which also strips out most volatile species which then have to be captured and safely disposed of.

It was recently discovered that nuclear reactors can be designed with molten salt fuel held in fuel assemblies very similar to those in uranium oxide or uranium metal fuelled reactors with no pumping of the molten fuel required. Fission product gasses in oxide fuel are trapped as very high pressure microbubbles in the fuel while they are released from metal fuel and accumulate to relatively high pressure in the fuel cladding. Early attempts to allow these gasses to vent into the reactor coolant in the Dounreay Experimental Fast Reactor had to be abandoned due to the high proportion of the hazardous and volatile fission product caesium which was released into the coolant [1].

Molten salts could in principle trap such volatile fission products much more effectively than is the case with metal fuel. It was therefore of interest to determine what the composition of the gas stream released from molten salt fuel would be and whether that composition would be consistent with simple venting of the gas into the coolant.

METHODS

The chemical composition of partially burned molten salt fuel was calculated as follows. The initial fuel composition was 60mol% NaCl, 20mol% PuCl₃, 20mol% UCl₃. It was assumed that 5mol% of fissile isotopes fissioned producing 10mol% fission products and higher actinides in the proportion found in spent fast reactor fuel [2]. The resulting composition is given in table 1. Na and the actinides are given as chloride salts, all fission products are presented as elements with 15mol% of Cl added to represent the chlorine released from 5mol% fissioned actinide trichlorides.
The equilibrium composition of this mixture as a function of temperature, at a constant 1 bar pressure, was calculated using HSC Chemistry 8. This program (unlike earlier versions) is able to handle the very large number of possible compounds originating from the 39 elements present in the fuel. The equilibrium composition was calculated by Gibbs Free Energy minimisation. The standard thermochemical database included with the software was used with the addition of data for the complexes of NaCl with ZrCl4 which were not present in that database and were estimated using the estimate function in the software.

Excess zirconium metal was included in the composition to represent the sacrificial metal provided in the fuel tube which controls the fuel salt redox potential. Without that sacrificial metal, significant amounts of UCl4 and iodine are present in the gas produced (data not shown).

<table>
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<tr>
<th>Moles</th>
<th>Element</th>
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<td>MO</td>
<td>11.28</td>
<td>SE</td>
<td>0.24</td>
<td>Total</td>
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Table 1 Composition of molten salt fuel after 5 mol% burnup

RESULTS

The design of the fuel tube is illustrated in figure 1. Approximately ¾ of the tube is filled with molten fuel salt with the upper region left as a gas space. The gas space is divided into two regions, a lower simple tube and an upper “diving bell” apparatus that allows gas to vent but prevents coolant entering the fuel tube. That design is taken from that proposed for vented metal fuel by GE [3] and is related to that used in the Dounreay Experimental Fast Reactor [1].

The fuel salt has a surface temperature of approximately 1000°C while the walls of the upper regions of the tube are at the coolant temperature of approximately 600°C. Vapour from the molten salt therefore
partially condenses on the tube walls.

The major fission gasses are the noble gasses, xenon and krypton. These have low solubility in the molten salt and, unusually, have higher solubility at higher temperatures [3]. The consequence is that they will form bubbles within the salt primarily in regions of lower temperatures. The rate of production of these gasses can be calculated from the average power density of the fuel salt as follows.

Average power = \(250\text{kW/l} = 250,000 \text{J.s}^{-1}\text{l}^{-1} = 6.24 \times 10^{12} \times 250,000 \times 3600 = 5.6 \times 10^{21} \text{MeV.hr}^{-1}\text{l}^{-1}\)

Fission energy = 200MeV

Fission rate = 2.8 \times 10^{19} \text{fissions.hr}^{-1}\text{l}^{-1}

Noble gasses produced at 0.23 mol per fission

Gas production rate = \(2.8 \times 10^{19} \times 0.23/(6.023 \times 10^{23}) = 1.1 \times 10^{-5} \text{mol.hr}^{-1}\text{l}^{-1}\)

Volume of gas = \(1.1 \times 10^{-5} \times 22400 = 0.25\text{ml.hr}^{-1}\text{l}^{-1}\) at NTP

Volume of gas at 600°C = \(0.25 \times 873/293 = 0.74\text{ml.hr}^{-1}\text{l}^{-1}\)

For a fuel tube where the gas space is \(\frac{1}{4}\) of the total, this corresponds to generating one gas space volume each 14 days. Flow of gas through the gas space is therefore slow enough to make the assumption that condensation of the gas evolved from the hot salt on the cooler tube wall will reach equilibrium.

The composition of the gas released from the fuel tube is therefore calculated by first calculating the composition of the gas released in bubbles from the fuel salt, assuming that this happens at a temperature of 1000°C – a pessimistically high temperature given that the noble gasses will bubble out in the coldest area of the fuel salt. Then this gas is allowed to condense at 600°C and the gasses remaining are those ultimately released through the gas vent.

Figures 2 (linear scale) and 3 (log scale) show the composition of the gas before and after condensing. Of particular note are the extremely low levels of hazardous cesium and iodine in the gas leaving the fuel tube. Almost no cesium and just 0.004% of the iodine is lost from the fuel tube. Apart from the noble gasses (which are discussed below) the only significant releases are of ZrCl\(_4\) and Cd. Both Zr and Cl will contain radioactive isotopes. However the coolant salt is already contaminated with those isotopes which are produced by neutron activation of the ZrF\(_4\) in the coolant and by the (n,a) reaction on KF in the coolant. The released ZrCl\(_4\) therefore does not significantly increase the hazard or the disposal challenge of the coolant salt.

![Figure 2 Composition of gasses before and after condensing](image-url)
Cadmium contains a number of radioactive fission products, $^{113}$Cd, $^{113m}$Cd, $^{115}$Cd and $^{116}$Cd. The 113 and 116 isotopes are naturally occurring and extremely low radioactivity. $^{115}$Cd is produced in only trace amounts in fission reactors and has a half life of 53 hours and so will largely decay before leaving the fuel tube. $^{115m}$Cd has a longer half life (44 days) but is produced in very low yield and is mostly destroyed in the fuel due to its very high neutron capture cross section. The radiological risk associated with the cadmium gas release is therefore minimal.

The release of the noble gasses needs to be considered from a radiological perspective. There are two potential hazards, one from direct radiation from decay of the noble gas and one from radioactive decay products of those gasses.

Krypton contains only one radioactive isotope $^{85}$Kr. This has a 10.76 year half life but a low radiological hazard due to its biological inertness. It is routinely released to atmosphere during nuclear fuel reprocessing and decays to non-radioactive Rb.

Xenon has several radioactive isotopes. Per se, they have similar low biological hazard as krypton, but certain isotopes decay to radioactive cesium isotopes which have a high biological hazard due to accumulation in bones. Indirect release of radioactive cesium from the fuel tube via xenon is therefore an issue that must be addressed.

The fuel tube described in figure 1 has, in effect, three gas compartments – the fuel salt itself, the main gas space in the tube and the gas space in the diving bell vent. Flow of gas is essentially unidirectional due to the small surface area of the fuel salt and the capillary between the main gas space and the vent space. The residence time of the gas in each space is long enough for the gas to fully mix.

That allows the decay of the radioactive gas to be modelled as it flows through the three compartments and then out into the coolant salt.

For a compartment of volume V, with a flow rate of $f$ ml/hr, a half life of $h$ hours then the ratio of the radioactivity flowing into the space with that flowing out is given by the equation

$$\text{Ratio of radioactivity in/out} = \frac{(V - V*0.5^{t/h} + f*t)}{(f*t)}$$

This solution converges to the correct ratio as $t$ approaches zero.
Application of this equation to the three “gas” compartments in the fuel tube gives the results shown in table 2.

<table>
<thead>
<tr>
<th></th>
<th>Half life (hr)</th>
<th>% escape salt</th>
<th>% escape tube</th>
<th>% escape vent</th>
<th>Fraction escaping overall</th>
</tr>
</thead>
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<td>$^{133}$Xe</td>
<td>125.94</td>
<td>99.55193</td>
<td>39.42738</td>
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<td>$^{138}$Xe</td>
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<td>26.58122</td>
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</table>

Table 2 Decay of xenon isotopes passing through the fuel tube

$^{133}$Xe decays to stable $^{133}$Cs and therefore represents no danger. $^{135}$Xe decays to $^{135}$Cs which has very low radioactivity with low energy β decay and no gamma radiation. Only 0.7% of this isotope escapes from the fuel tube. $^{137}$Xe decays to the very hazardous $^{137}$Cs but only 40 billionths of this isotope escape from the fuel tube. $^{138}$Xe is produced in only minute quantities in fission and only 1 millionth escapes the fuel tube.

It can therefore be concluded that indirect release of dangerous isotopes from the fuel tube via the vented noble gasses is so small as not to be a significant safety issue.

CONCLUSIONS

A chloride based uranium/plutonium fuel salt mixture can be placed into vented fuel tubes in a nuclear reactor. The gas vented from the tubes contains only trace amounts of biologically hazardous isotopes such as iodine and cesium or their volatile radioactive precursors and does not create significantly troublesome contamination of the coolant salt.

Vented fuel tubes are therefore practical with the molten salt fuel, and indeed are desirable since venting reduces the probability of fuel tube leakage. The problem of venting of dangerous radioactive species that made tube venting in metal fueled sodium fast reactors does not exist with the molten salt fuel due to the different chemistry of metallic uranium and uranium chloride salts.

ACKNOWLEDGMENTS

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REFERENCES