

Uranium Hydride: Formation, properties and reaction with water

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Completed on behalf of Sellafield Ltd.

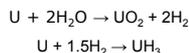
Introduction

In some waste-streams containing metallic uranium (e.g. Magnox fuel) conditions suitable for the formation of uranium hydride may exist. During waste treatment any hydride formed could potentially ignite on exposure to air or react violently on exposure to liquid water. This potential may have important implications for safety cases and waste recovery operations.

The National Nuclear Laboratory has recently completed a programme of research for Sellafield Limited that investigated the conditions required for the formation and persistence of uranium hydride and the reactivity of the material formed.

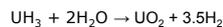
Background

In principle, uranium hydride may be formed wherever uranium metal comes into contact with water, by reaction of the metal with hydrogen formed by corrosion of the uranium (or other metals in the system):



Uranium hydride can be pyrophoric, reacting very vigorously with atmospheric oxygen. Small fires at Argonne & Lawrence Livermore laboratories have been ascribed to corrosion product containing uranium hydride reacting with air.

If further water is present, uranium hydride can also be destroyed by hydrolysis:



The objectives of this work were to examine the formation of uranium hydride across a range of conditions and to determine the rate of reaction between uranium hydride and water. This information, together with determination of the rate of water transport through the storage media, can be used to estimate whether reactive uranium hydride may persist under a given storage regime.

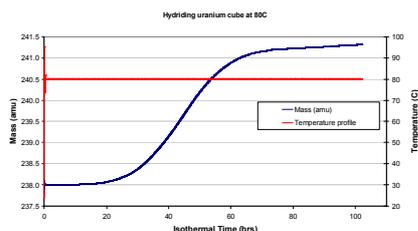
Preparation of Uranium Hydride

Uranium hydride was prepared in two thermogravimetric analysers, under two regimes. In both cases Magnox-grade uranium metal in the form of 5mm cubes was reacted with a continuous flow of hydrogen gas, diluted in argon.

In the first set of trials the simultaneous formation and hydrolysis of uranium hydride was studied by the reaction of uranium cubes with 25% hydrogen in argon containing 400-6000ppm water vapour. Hydride formation was carried out across a range of temperatures from 65°C to 160°C. Hydride could be formed at 65°C even in the presence of moderately high levels of oxygen (85-150ppm) and water vapour (1000-5200ppm).

The second set was carried out using a TGA located in an inert-atmosphere glovebox using 2.5% hydrogen in argon. Sub-ppm oxygen levels and water levels as low as 20ppm were achieved. In these trials hydride was formed at temperatures as low as 30°C, and as high as 200°C.

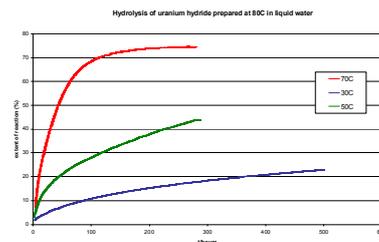
The increase in mass as hydride was formed showed an induction period, where the change in mass was immeasurably small, followed by a gradually increasing rate and then by a gradual decrease in rate as the metal was consumed. The rate profile and absolute rates were completely consistent with literature results for this reaction.



Reaction of Uranium Hydride with Water

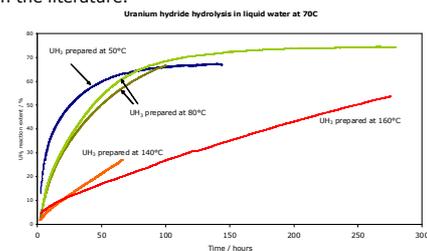
The reaction of uranium hydride with any remaining water within the storage environment will have a strong bearing on its likely persistence. Hydrolysis of uranium hydride was therefore studied with both liquid water (in an isothermal calorimeter) and water vapour (in the TGA located in the inert-atmosphere glovebox).

The reaction with liquid water showed the expected increase in rate at higher temperature of reaction:



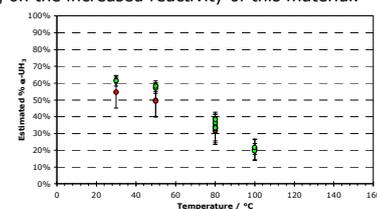
The rate showed a significant decrease at approximately 75% extent of reaction, although hydrogen production was still measurable. This result has been reported previously.

The rate also showed a very significant dependence on the temperature at which the hydride had been made. This effect has not previously been described in the literature.



Surface area measurements (by krypton sorption) showed that the difference in the reactivity was not due to a significant difference in the surface areas between hydride samples prepared at different temperatures.

Uranium hydride can exist in two crystalline forms. The phase composition of hydrides prepared at various temperatures was measured using powder X-ray diffraction and the method of standard additions. Hydride prepared at lower temperature contained a larger proportion of the alpha phase. This may have some bearing on the increased reactivity of this material.



Conclusions

Extrapolation of results obtained using uranium hydride prepared at high temperatures to hydride formed at temperatures more typically experienced during, for instance, uranium fuel storage may need to be carried out with caution.