ABSTRACT

A corrosion cycle for uranium is postulated which can be used to assess whether a given storage situation might produce fire hazards and/or continual uranium corrosion. A significant reaction rate of uranium and moisture occurs at room temperature which produces uranium oxide and hydrogen. If the hydrogen cannot escape, it will react slowly with uranium to form uranium hydride. The hydride is pyrophoric at room temperature when exposed to air. Either the hydrogen or the hydride can produce a dangerous situation as demonstrated by two different incidents described here. Long-term corrosion will occur even if the normal precautions are taken as is demonstrated by the long-term storage of stainless steel clad uranium fuel plates. The major initiator of these problems is attributed to any moisture condensed on the metal or any brought in by the cover gas. The postulated corrosion cycle is used to suggest ways to circumvent these problems.

I. INTRODUCTION

The long-term storage of uranium near room temperature can result in fire hazards and/or continual uranium corrosion. Uranium itself, especially in large pieces, is not pyrophoric at room temperature but the powdered hydride and hydrogen that forms from the reaction of water vapor and uranium is pyrophoric and combustible. Examples of undesirable events which occurred as a result of these hazards are described in this paper and explained in terms of a postulated Corrosion Cycle which is verified experimentally. If the corrosion cycle is understood, then long-term storage can be accomplished without significant corrosion or fire danger.

An incident which illustrates the fire hazard occurred at Oak Ridge National Laboratory in 1992. It resulted in the contamination of an employee from a small U-235 fire. The fire was initiated by opening a bottle containing uranium foil.

Corrosion problems (and some flashing) are demonstrated from experience with long-term storage (ten years) of Zero Power Physics Reactor (ZPPR) U-235 fuel plates at Argonne National Laboratory. Until recently, corrosion of these plates continued despite attempts to mitigate the problem.

Another incident shows that the uranium reaction with moisture can produce enough hydrogen to cause a mild explosion.

II. POSTULATION OF THE CORROSION CYCLE

The basis of the corrosion cycle is the existence of water vapor in the atmosphere used to prepare or store uranium in closed or vented containers. Use of an inert atmosphere to store uranium can be even worse than storing it in air. The reason is that the oxygen in air will produce a protective oxide layer on the fuel to slow down the reaction with moisture but the moisture in an inert gas is not impeded by this restraint. Water vapor will react with the metal to produce UO₂ and hydrogen according to the reaction

\[ U + 2 \text{H}_2\text{O} \rightarrow 2 \text{UO}_2 + 2 \text{H}_2 \]  

Richie presents the reaction rates of both oxygen and water vapor with uranium and shows that the reaction rate of the water vapor with uranium is faster than oxygen is. It is very difficult to obtain a perfectly dry gas to store the fuel in. Attempts to use argon as the cover gas have proven unsuccessful because of the difficulty of obtaining it perfectly dry.

The next step in the corrosion cycle depends upon whether the storage container is vented or not. If it is
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vented, then the hydrogen can escape and corrosion will continue as long as there is moisture in the cover gas. Care must be exercised with the hydrogen produced since it can cause damage\(^5\). If the container is not vented, the hydrogen will react with the uranium to form uranium hydride according to the reaction

\[
2 \text{U} + 3 \text{H}_2 \rightarrow 2 \text{UH}_3
\]  

(2)

The uranium hydride is a loose fine black particulate. The rate of this reaction appears to be slow and is accompanied by an incubation period especially if an oxide is also forming or formed\(^6\).

If oxygen is present, it reacts quickly and sometimes violently with the uranium hydride to produce more water and uranium oxide according to the reaction

\[
2 \text{UH}_3 + 3.5 \text{O}_2 \rightarrow 2 \text{UO}_2 + 3 \text{H}_2\text{O}
\]

(3)

The \(\text{UO}_2\) is in the form of powder because the \(\text{UH}_3\) was a powder. Thus, this process turns the metal into a metal oxide powder. Hartmann\(^5\) discusses the pyrophoricity of uranium hydride and states that the explosive limits of the powder in air is from 45 to 300 mg/liter. Stakebake\(^6\) reports that the hydride of plutonium also reacts violently under certain conditions.

### III. RECOMMENDATIONS BASED UPON THE CORROSION CYCLE

Removal of all cover gas would stop undesirable reactions but vacuum storage may be impractical because of the difficulty of maintaining a vacuum over a long time. Continual vacuum pumping will remove any hydrogen produced.

If oxygen is not present, such as with argon or helium cover gas in a closed system, reactions 1 and 2 will continue until the water and hydrogen produced are used up. This leaves one reactant product, \(\text{UH}_3\). If oxygen is suddenly introduced, the reaction with the hydride can be violent. Obtaining a completely dry cover gas may be difficult but might still be practical. If some corrosion is acceptable, then venting the system to relieve the hydrogen produced is necessary.

If oxygen is present in the cover gas in a closed system, reactions 1, 2, and 3 will continue until all the oxygen, water, and hydrogen are used up. Reaction 2 will be the final reaction so that the hydride still remains and the end state is similar to that mentioned above. In both cases, if the canister was initially filled with atmospheric air, the final pressure will be reduced because the oxygen is removed from the gas phase.

If the container leaks, with the reduction in the pressure due to consumption of oxygen, air will continue to leak into the gas space and the added oxygen will be used up by reacting with the hydride according to the above corrosion cycle. This process will continue until the gas phase consists of nitrogen at atmospheric pressure. Even after pressure equalization, a small amount of air can diffuse into the canister and pumping from atmospheric pressure changes could cause some interchange of nitrogen out and air in but both of these are small effects. Movement of the canisters when there is only nitrogen left in the cover gas presents no hazard except that the fine particles (uranium oxide and uranium hydride) within the canister will spread out making contamination and spontaneous ignition more probable when the canister is opened.

If the canisters are moved when there is still oxygen in the canister, then an explosion hazard exists since the \(\text{UH}_3\) can react pyrophorically. The uranium hydride dust can be suspended in the air in the canister, and if the canister is closed, explosive forces could occur\(^6\). Thus, the canisters should not be moved when there is oxygen remaining unless due caution is exercised so that the particles in the canisters would not be suspended.

If the canisters are opened for final disposal of the uranium, due care must be exercised to not suspend the uranium hydride dust or it will flash. Opening the cladding will likely cause such flashing unless done in an argon filled glove box. Contamination spread is also a likely possibility because of the fine particle form of the oxide produced from the \(\text{UH}_3\).

In either case, the result is a container with a fire or explosion hazard from the uranium hydride powder when and if the container is opened to air. In effect, hydrogen molecules in the water that is introduced either initially or in the cover gas remains in the system to react over and over again as long as the hydrogen is not released from the system. Essentially, the hydride never disappears during storage even though oxidation proceeds.

### IV. APPLICATION OF CORROSION CYCLE TO PAST EVENTS

In a closed container, after the corrosion cycle proceeds as far as it can, the above corrosion cycle produces a cover gas containing only inert gas such as nitrogen but, unfortunately, also uranium hydride in a hazardous powder form.

#### A. Uranium Fire at Oak Ridge

In the case of the fire at Oak Ridge, a bottle with uranium foil was sealed with air containing atmospheric
moisture. The water vapor and oxygen were totally consumed according to reactions 1, 2, and 3, leaving only U, UO₂, UH₄, and a reduced pressure cover gas containing only nitrogen. When the bottle was opened, air rushed in due to the reduced pressure. The hydride reacted immediately with the oxygen and released enough heat to cause the uranium to reach its ignition point and burn.

B. Corrosion of ZPPR Fuel Plates at Argonne

Stainless steel clad enriched uranium fuel plates for the ZPPR at Argonne National Laboratory are stored in rectangular canisters. Most of the fuel elements are 1/16"x2"x6" nominal dimensions and 16 to 32 plates can be stored in each canister. The cladding is vented on both ends so that the gas atmosphere in the canister does communicate with the fuel.

In 1985, corrosion of the ZPPR enriched uranium fuel plates was discovered. The initial corrective action was the placement of desiccant packets in the storage canisters to eliminate the water. In 1990, continuation of the corrosion was observed. A study showed that the desiccant failed because it was not an irreversible chemical reaction and uranium had the greater affinity for water. The corrective action instituted in 1990 was to flush each canister with dry air and then evacuate the canisters. In 1993, further corrosion was observed.

Over the years of storage until 1993, approximately 1500, or 20% of the total number of plates, were rejected for further use because of either ruptured or deformed cladding. The deformation is caused by the conversion of the uranium to powdered uranium oxide by the corrosion cycle. This deformation mechanism was also described in a recently declassified report on fuel element ruptures in water and steam. The ones with ruptured cladding, approximately 10% of the reject plates, were wrapped in plastic. The identification of hydrogen and the depletion of oxygen in canisters containing only non-deformed plates confirms that corrosion is occurring even in these plates.

As mentioned above, the attempt to stop the corrosion of the ZPPR plates in 1990 consisted of evacuating the canisters containing the uranium fuel plates. The design of the canister was not adequate to maintain a vacuum in most of the canisters. Over the period of a year, most canisters leaked enough air to return to atmospheric pressure and the plates continued to corrode until all the oxygen was consumed and only nitrogen at atmospheric pressure remained in the cover gas. After a year, per procedure, the canisters were pressure checked, and re-evacuated. This pressure check and re-evacuation provided a fresh supply of oxygen to the canister annually, allowing the corrosion to continue.

The intermediate solution adopted in 1993 based on the corrosion cycle was to leave the canisters untouched since several instances of flashing had occurred in opening these canisters and since the leakers would end up with a nitrogen environment near atmospheric pressure and the corrosion would stop. Initial moisture in the canned fuel plates is postulated to be a principal step in the corrosion process. Therefore, plates which had not corroded significantly would not be expected to in the future unless exposed to moisture.

Further plans were made to permanently store this fuel and these will be described later. However, to make certain that the conclusion concerning the corrosion cycle applied in this case, the atmospheres of five of the canisters were analyzed for composition. Two canisters contained "reject plates" and the other canisters contained "good plates". Table I gives the identification of each canister, evacuation and sample dates, and the measured pressures.

<table>
<thead>
<tr>
<th>Canister No.</th>
<th>Date Evacuated</th>
<th>Date Sample</th>
<th>Pressure Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>82U R*</td>
<td>4/12/91</td>
<td>9/24/92</td>
<td>620</td>
</tr>
<tr>
<td>87A R</td>
<td>5/23/91</td>
<td>9/29/92</td>
<td>557</td>
</tr>
<tr>
<td>87M G**</td>
<td>4/5/91</td>
<td>9/29/92</td>
<td>478</td>
</tr>
<tr>
<td>90C G</td>
<td>4/1/92</td>
<td>10/1/92</td>
<td>234</td>
</tr>
<tr>
<td>72C G</td>
<td>4/16/91</td>
<td>10/1/92</td>
<td>536</td>
</tr>
</tbody>
</table>

Average Atmospheric Pressure = 637 Torr
* Reject plates
** Good plates

Clearly, each canister allowed air to leak in. In the 5 or 6 months, the pressure had reached almost local atmospheric pressure in one canister, in the range of 500 torr for the three others, and about one third of an atmosphere in the remaining canisters. The composition of the atmosphere in each canister was measured by gas chromatography. The results of the measurements are given in Table II.

The analyses show that the atmospheres are rich in nitrogen and that oxygen has been almost completely depleted in all canisters. These results are consistent with the corrosion cycle. In one canister, the lowest pressure, a significant amount of hydrogen has been produced and remains showing that the formation of the hydride has been inhibited. This may be due to the effect of pressure on reaction rate. In any case, introduction of air into this
Table II. The Results of the Analysis of Canister Atmospheres

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ambient Air</th>
<th>82U(R)</th>
<th>87A(R)</th>
<th>Canister 87M(G)</th>
<th>90C(G)</th>
<th>72C(G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ v/o</td>
<td>0.00005</td>
<td>0.63</td>
<td>0.16</td>
<td>0.28</td>
<td>13.34</td>
<td>4.99</td>
</tr>
<tr>
<td>Ar v/o</td>
<td>0.93</td>
<td>1.13</td>
<td>1.14</td>
<td>1.13</td>
<td>0.98</td>
<td>1.08</td>
</tr>
<tr>
<td>O₂ v/o</td>
<td>20.9</td>
<td>0.12</td>
<td>0.15</td>
<td>0.21</td>
<td>0.60</td>
<td>0.11</td>
</tr>
<tr>
<td>CO₂ v/o</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>N₂ v/o</td>
<td>78.1</td>
<td>95.3</td>
<td>96.0</td>
<td>95.1</td>
<td>81.0</td>
<td>91.6</td>
</tr>
<tr>
<td>CH₄ v/o</td>
<td>0.0002</td>
<td>&lt;0.06</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
</tbody>
</table>

The reaction would produce an explosive mixture of hydrogen and oxygen.

C. Storage of Depleted Uranium

The Fernald Environmental Management project reported that two drum lids on containers used for permanent storage of depleted uranium blew off on June 19, 1992. The lids probably blew off because of hydrogen produced in the corrosion cycle which reacted with the air in the containers. The reaction was probably set off by a spark. The depleted uranium is stored in a small drum inside two larger ones and none of the material was exposed. The drums are vented to allow the hydrogen to escape but the ventilation system apparently malfunctioned^1.

V. LESSONS LEARNED APPLIED TO THE STORAGE OF ZPRR FUEL

The corrective action selected for final storage of the plates is utilization of an irreversible hydrogen-oxygen-water getter in an ultra-dry nitrogen atmosphere. The nitrogen atmosphere would be sufficient if the canisters sealed perfectly. However, some pumping is expected due to changes in atmospheric pressure. For the small amounts of air pumped into the canisters, the getter will remove the potential reactants before further corrosion occurs.

The hydrogen-oxygen-water getter consists of a packet of unsaturated hydrocarbon containing a palladium catalyst and a packet of lithium hydride. Hydrogen, water and oxygen are eliminated by the reactions:

\[ H_2 + LiH \rightarrow Li OH + H_2 \] (4)

\[ 2H_2 + O_2 \rightarrow 2H_2O \] (5)

\[ PD \]

\[ 2H_2 + (\text{CH}_2) \rightarrow (\text{CH}_2 \text{OH}) \]

\[ \text{Cat} \]

There are 231 canisters containing a mix of usable and unusable enriched uranium fuel plates. Approximately 3 months were spent sorting these plates into usable and reject canisters. Plates were rejected if the clad swelling due to hydration and/or oxidation was greater than 0.03 in. above the normal plate surface. In a large number of plates, the swelling had ruptured the cladding. These plates were wrapped in aluminum foil to prevent the spread of contamination. As mentioned previously, many ruptured plates discovered in previous inspections were wrapped in plastic. DOE regulations require excess combustibles to be removed from storage containers. Therefore, the plastics were removed and these plates were wrapped in aluminum foil. After the plates were sorted and, if necessary wrapped in aluminum foil, packets of getter were placed in each canister and they were evacuated and backfilled with ultra-dry nitrogen.

Table III summarizes the number of usable, rejected, and the percent rejected by size. Thus, it is seen that over the ten years of storage, over 25 percent of the plates have deformed or ruptured.

Currently, the atmosphere inside several canisters is being checked each month for hydrogen and oxygen. Physical inspections of the usable plates will be performed as part of the DOE annual inventory. The monthly inspection of selected canisters has shown no signs of additional corrosion or deterioration of getter packets and no oxygen and hydrogen concentration greater than 0.1 percent for the last nine months.
Table III. Enriched Uranium Plate Summary

<table>
<thead>
<tr>
<th>Size (in.)</th>
<th>Usable (number)</th>
<th>Rejects (number)</th>
<th>Rejects (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/16 x 2 x 8</td>
<td>870</td>
<td>450</td>
<td>34.1</td>
</tr>
<tr>
<td>1/16 x 2 x 6</td>
<td>2744</td>
<td>1118</td>
<td>28.9</td>
</tr>
<tr>
<td>1/16 x 2 x 4</td>
<td>944</td>
<td>373</td>
<td>28.3</td>
</tr>
<tr>
<td>1/8 x 2 x 8</td>
<td>161</td>
<td>59</td>
<td>26.8</td>
</tr>
<tr>
<td>1/8 x 2 x 6</td>
<td>515</td>
<td>142</td>
<td>21.6</td>
</tr>
<tr>
<td>1/8 x 2 x 4</td>
<td>151</td>
<td>56</td>
<td>27.1</td>
</tr>
</tbody>
</table>

VI. CONCLUSIONS

The corrosion cycle postulated in this paper is useful for predicting the conditions which will lead to problems in storing uranium. The cycle was confirmed by measurements made in the storage of ZPPR uranium fuel plates at Argonne National Laboratory. The chemical analysis of the atmosphere in five canisters showed that one of them had a significant amount of hydrogen which could be susceptible to burning. An incident at Fernald showed that hydrogen production can be dangerous if it is not properly vented. An incident at Oak Ridge showed that the consumption of air and water vapor in a closed container can produce a hydride residue at low pressure and that a container opened at this reduced pressure can cause enough air to rush in to cause a fire.

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REFERENCES


