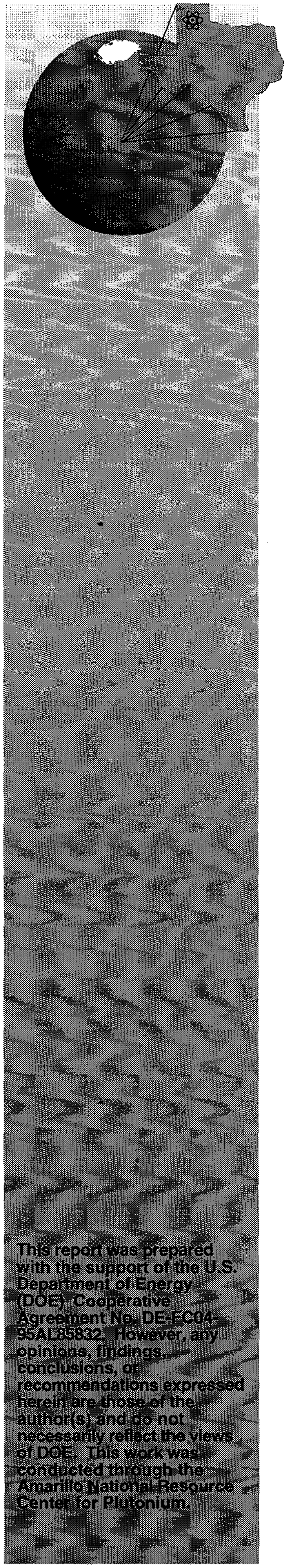

Amarillo National Resource Center for Plutonium

A Higher Education Consortium of The Texas A&M University System,
Texas Tech University, and The University of Texas System

Investigations in Gallium Removal

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INVESTIGATIONS IN GALLIUM REMOVAL

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Abstract

Gallium present in weapons plutonium must be removed before it can be used for the production of mixed-oxide (MOX) nuclear reactor fuel. The main goal of the preliminary studies conducted at Texas A&M University was to assist in the development of a thermal process to remove gallium from a gallium oxide/plutonium oxide matrix. This effort is being conducted in close consultation with the Los Alamos National Laboratory (LANL) personnel involved in the development of this process for the US Department of Energy (DOE). Simple experiments were performed on gallium oxide, and cerium-oxide/gallium-oxide mixtures, heated to temperatures ranging from 700 - 900 °C in a reducing environment, and a method for collecting the gallium vapors under these conditions was demonstrated.

Background

The scope of DOE's integrated approach for weapons component conversions includes two options for plutonium disposition: (1) immobilization via vitrification/ceramification, or (2) use of the plutonium for fabrication of mixed uranium/plutonium oxide (MOX) fuel for commercial nuclear power reactors. However, weapons-derived plutonium contains approximately 1 weight percent gallium. Gallium at such concentrations presents various issues for MOX fuel fabrication and use. MOX fuel is a ceramic material, prepared by sintering oxides of uranium and plutonium, which are initially both in the form of fine powders. At high concentrations, gallium affects the sintering behavior of the ceramic. Since plutonium weapon components do not all have the same concentration of gallium, the sintering process parameters would have to be adjusted as the gallium concentration changed (undesirable in an industrial-scale operation) unless the gallium was reduced to an acceptable level prior to fabrication. In addition, there may be issues with using MOX fuel with excessive gallium concentration as a reactor fuel due to the potential effect of gallium on the fuel cladding. Therefore, its concentration must be reduced if the MOX option for plutonium disposition is pursued.

For the past few years, researchers at LANL have been developing a dry thermal process for removing the gallium from the plutonium oxide feed for use in MOX fuel fabrication[1,2]. The LANL research has demonstrated the ability of this process to reduce gallium concentrations to less than 150 ppm in the plutonium oxide feed[2] and to approximately 4 ppm in the final MOX fuel[3]. However, in the gallium removal studies conducted at LANL, the gallium was not collected as it evolved from the plutonium oxide matrix. This resulted in deposits of gallium collecting on the furnace surfaces[3], an undesirable side effect due to gallium's corrosive nature. The research described in this report compliments the LANL efforts by demonstrating a simple method for collecting the gallium during the removal process, thus eliminating this problem.

The thermal gallium removal process involves using a reducing atmosphere to reduce the fully-oxidized state of gallium, gallium trioxide (Ga_2O_3), which is produced during the conversion of the plutonium metal to oxide, to gallium suboxide (Ga_2O), and then distilling the volatile gallium suboxide from the plutonium oxide (PuO_2) matrix. Cerium oxide (CeO_2) is a good surrogate for PuO_2 for the studies involving ceramic phases. Thus, the removal of gallium from a PuO_2 matrix can be studied using small amounts of Ga_2O_3 well-mixed in a CeO_2 matrix.

Using the background described above, researchers at Texas A&M University developed an approach for the clean separation of metallic gallium from a gallium trioxide/plutonium oxide matrix. Volatile gallium suboxide is generated by heating the mixed matrix in hydrogen, and then the gallium is collected as a metal by reducing the gaseous gallium suboxide on a copper surface. Copper acts as a catalyst which reduces gaseous gallium suboxide to virtually nonvolatile liquid gallium, which, in turn, solidifies at room temperature allowing for easy handling and disposal. A few experiments using cerium oxide as a surrogate for plutonium oxide were conducted to test the validity of this approach. The experiments demonstrated that gallium metal is recovered from the gallium trioxide/cerium oxide matrix and gallium is deposited only on the designated copper surface.

Procedure

Gallium (III) oxide (99.999%; Avocado Research Chemicals Ltd.) and Cerium (IV) oxide (99.9%, < 5 microns; Aldrich Chemical Company) were used for the gallium removal experiments. The first series of experiments used about 500 mg of pure gallium trioxide and a 25 cm long copper wire weighing about 2 g. Reactor temperatures ranged from 500 to 900 °C. In each experiment, the oxide was heated in hydrogen at a constant temperature for about 8 hours, while infusing hydrogen at flow rates ranging from 5 to 10 ml/M. Instead of pure gallium trioxide, a mixture of 10% gallium trioxide in cerium oxide was used in another series of experiments. For these experiments, a homogeneous mixture of 10% gallium trioxide in cerium oxide was prepared using a mortar and pestle.

Figure 1 depicts the experimental setup. The glass shop in the Department of Chemistry at Texas A&M University made several "U" reactors from straight 60 cm long 6 mm o.d. quartz tubing. The reactors were about 25 cm tall with two side tubes separated by about 1.2 cm. Quartz wool plugs were used to position gallium trioxide in one side. Copper wire was placed in the other side. A gas regulator set at 5 psi controlled the supply of hydrogen. The flow of hydrogen was maintained by a metering valve. The hydrogen flow ranged from 5 to 10 ml per minute. A 1/8" stainless steel tube was used for the hydrogen supply line, which was connected to the inlet side of the quartz reactor using a piece of Tygon tubing. Another piece of Tygon tubing was used to connect a

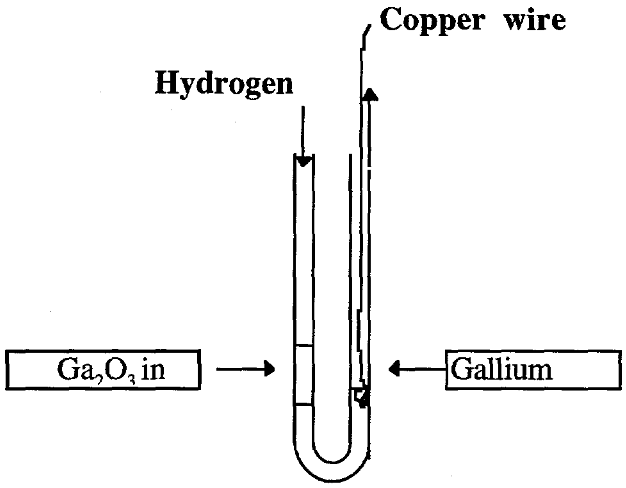

Figure 1. Apparatus Used for Gallium Removal Experiments.

soap bubble meter to the exit side of the quartz reactor. The quartz reactor was placed in a furnace (Lindberg \ Blue M) through a hole in the top of the furnace and the reaction was then initiated. About 8 cm of quartz tubing was outside the furnace to keep the Tygon tubing from melting.

The use of Tygon tubing was only a temporary solution until a better gas manifold using suitable glass-to-metal connectors was assembled. Tygon tubing is not at all desirable for long-term iterations of experiments such as these, and the researchers recognize that it should be used with extreme caution and only on a temporary basis.

The quartz reactor and the furnace were operated inside a laboratory hood while under constant observation. A gas manifold was used to pass the gas through the matrix containing gallium trioxide first and then through the other side holding the copper wire.

The exit gas flow through the reactor outlet was measured before placing the reactor in the furnace and was measured periodically after placing the reactor in the furnace using the bubble meter. The reactor was heated in the furnace while infusing the reducing gas. About twenty experiments were conducted to explore the thermal technique for separating gallium from the cerium oxide.

The gallium removal was monitored indirectly because the analytical techniques for monitoring the gallium level in a solid metal oxide matrix were not readily available. Gallium deposited on the copper wire was used as an indication of gallium removal from the bed. The bubble meter used to monitor the flow of hydrogen through the quartz reactor was also used to monitor the hydrogen consumption rate during the reaction. It was assumed that there was no reaction at room temperature. As the reactor was heated above 700 °C, the hydrogen flow at the exit showed a decrease, although the inlet flow remained constant. The difference between the inlet and outlet flow rates was used to calculate the amount of hydrogen consumed during the reduction of gallium trioxide. It was also assumed that each mole of gallium trioxide consumes 3 moles of hydrogen. The researchers recognized that the Tygon tubing could have substantial leakage when the quartz reactor was heated. As a precaution against hydrogen leakage, the quartz reactor and the furnace were operated in a well-ventilated hood. If any leaks did occur, they were limited to the outside of the furnace as long as the quartz reactor was not broken, and were thus swept away by the air flow of the hood (100 CPM).

Results and Discussion

Formation of silvery droplets of gallium on the tip of the copper wire were observed when hydrogen was passed through the plug of gallium trioxide in a quartz reactor at temperatures ranging from 700 - 900 °C. On cooling, the droplets solidified at room temperature, indicating that the substance was pure gallium metal. Similar observations were made when an oxide mixture of 10% gallium trioxide in cerium oxide was used instead of pure gallium trioxide. Hydrogen is known to reduce gallium trioxide to gallium suboxide at temperatures above 580 °C following the process shown in Equation (1).

$$Ga_2O_3 + 2\ H_2 \rightarrow Ga_2O + 2\ H_2O \qquad (1)$$

The emitted Ga_2O and hydrogen gas then interacts with the copper in the manner shown in Equations (2) and (3).

$$Ga_2O + 2\ Cu \rightarrow Cu_2O + 2\ Ga \qquad (2)$$

$$Cu_2O + H_2 \rightarrow 2\ Cu + H_2O \qquad (3)$$

$$Ga_2O_3 + 3\ H_2 \rightarrow 2\ Ga + 3H_2O \qquad (4)$$

Consequently, by placing high surface area copper in the reactor, gallium in metallic form can be collected on the copper.

Figure 2 shows the consumption of hydrogen during gallium removal. Initially, the hydrogen flow was started through the quartz reactor with 10% gallium trioxide in cerium oxide before placing it inside the furnace at 900 °C, and the hydrogen flow at the exit decreased as the reactor temperature increased. The hydrogen flow increased continuously as it reacted with gallium trioxide in the oxide matrix. The experiment was not complete, however, and there was gallium left in the oxide matrix. In a similar experiment, hydrogen was passed through cerium oxide alone and the hydrogen flow rate did not change as the furnace temperature increased. From this information, two observations are that: (1) cerium oxide did not react with hydrogen and, (2) the system did not leak. Therefore, we conclude that the hydrogen was consumed by the gallium trioxide.

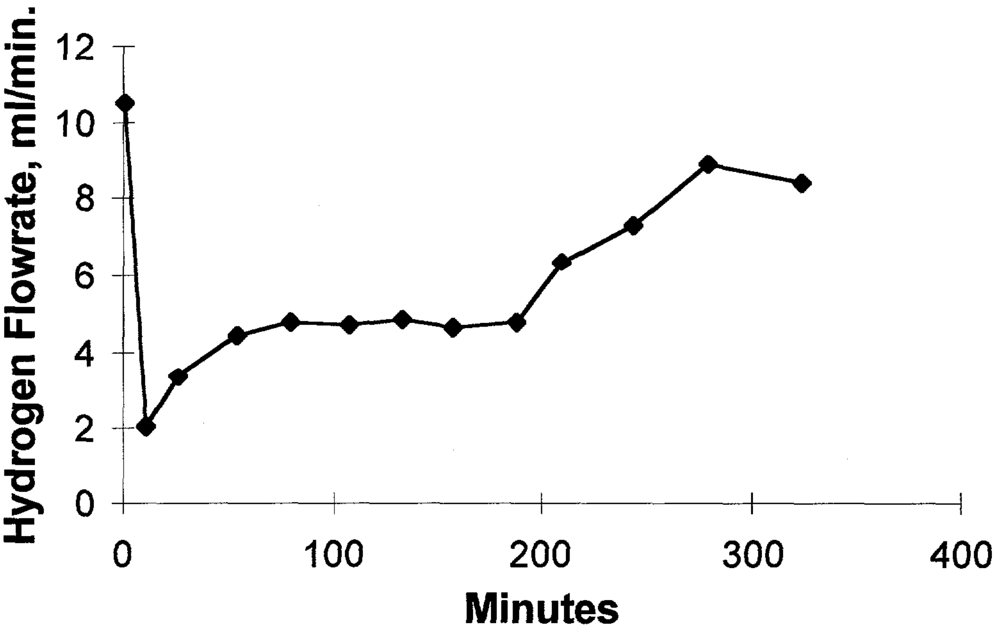

Figure 2. Hydrogen Consumption by 1 Gram Mixture of 10% Gallium Trioxide in Cerium Oxide at 900°C

Conclusion

The results of our preliminary study suggest that gallium from a gallium trioxide/plutonium oxide mixture can be removed and deposited as metallic gallium on copper metal placed inside the high temperature region of the gallium removal system, thereby eliminating the deposition of gallium on the surrounding surfaces. Future work will include demonstrating the concept on gallium removal from weapons-grade plutonium, and on developing this collection mechanism for use in a full-scale gallium removal system.

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