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A DIFFERENTIAL THERMAL ANALYSIS
STUDY OF THE EFFECT OF TRAMP
IMPURITIES ON THE EXOTHERMIC
 U_3O_8 - Al REACTIONS

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ABSTRACT

Differential thermal analysis (DTA) has been used to study the effect of impurities on aluminothermic reactions between commercial type 101 aluminum powder and U_3O_8 powder. No measurable effect (solid state reactions) was found below 660°C during differential thermal analysis studies of (1) loose blended powders, (2) blended and compressed powders, (3) blended, heated, and compressed powders, or (4) blended, compressed, and heated compacts containing less than 50,000 ppm impurities from group IA halide salts and group IIA oxides. It was determined that impurities (> 5 wt %) of alkali metal chlorides, and alkaline earth oxides, cause minor modifications of the reaction thermograms above 800°C for molten aluminum metal with U_3O_8 . It was also determined that attempts to prepare alkali, alkaline earth, and transition metal uranates under process conditions, via reaction of impurities with U_3O_8 prior to compaction with aluminum powder, also did not affect reactions below 660°C . In similar experiments where Fe_2O_3 and NiO were substituted for U_3O_8 , it was determined that $NaCl$ does modify the reactions between aluminum metal and Fe_2O_3 and between aluminum metal and NiO . With increasing $NaCl$ concentrations, the temperature for initiation of the reaction moves to lower temperatures. At 10 wt % $NaCl$, the exothermic "thermite" reactions between aluminum and Fe_2O_3 or NiO begin at approximately 640°C .

CONTENTS

Introduction 7

Summary and Conclusions 8

Background 9

Concerns 9

Prior Work on Al-U₃O₈ Reactions 10

Manufacturing of Aluminum-Uranium Oxide Fuel Tubes 12

Reject Tube Recycle 12

Impurities and Their Sources 15

Impurities in Type 101 Aluminum Powder 15

Impurities in U₃O₈ Feedstock 18

Impurities Introduced via Recycle of Reject Tubes 18

Impurities Introduced via Fission 18

Summary of Impurities 18

Experimental Procedure 22

Preparation of Cermet Samples 22

Preparation of Uranates under Simulated Process Conditions 22

Powder Metallurgy Tube Samples 22

Instrumental 22

Discussion and Interpretation of Results 23

Al-U₃O₈ Reactions 23

Classical Thermite Reactions 28

Metallothermic Reaction Modification via Impurities 28

NaCl as an Impurity 30

Other Impurities 35

Reactions of U₃O₈ with Various Impurities 41

Sample Preparation 41

Results of U₃O₈-Impurity Reactions 43

Metallothermic Reactions in Powder Metallurgy Tube Samples 43

Sample Preparation 43

Results of PM Reactions 49

References 51

A DIFFERENTIAL THERMAL ANALYSIS STUDY OF THE EFFECT OF TRAMP IMPURITIES ON THE EXOTHERMIC U_3O_8 -Al REACTIONS

INTRODUCTION

Fuel elements for nuclear reactors¹⁻³ contain uranium enriched in the isotope 235-uranium. The uranium is uniformly dispersed in a suitable matrix and is completely enclosed in a compatible cladding material. Low temperature nuclear reactors generally utilize aluminum or aluminum alloys for both the matrix and cladding materials. Fuel elements for the Savannah River Plant's (SRP) low- temperature heavy water (LTHW) reactors contain up to 30 wt % uranium in aluminum alloy that is extrusion-clad with aluminum metal. After irradiation and cooling, spent SRP fuel is dissolved, purified by solvent extraction, converted back to a uranium-aluminum alloy fuel, and then recycled back to the reactors.⁴

As a result of the neutron capture reaction, $^{235}U(n, g)^{236}U$, the ^{236}U concentration in the continually recycled enriched uranium stockpile in use at Savannah River has slowly increased over the years of operation.⁴ Although the rate of increase can be, and is, slowed by blending enriched uranium from alternate sources, the continual buildup of ^{236}U in the SRP stockpile of enriched uranium will eventually require increased uranium loadings for fuel elements. Manufacturing alloy fuel tubes with uranium loadings greater than about 35 wt % presents a number of seemingly insurmountable fabrication difficulties. The Savannah River Laboratory (SRL) has evaluated, tested, and proven an alternative cermet fuel form for the Savannah River reactors.⁵

The alternative fuel needed for uranium loading up to approximately 50 wt % is made by powder metallurgy (PM) methods and consists of U_3O_8 particles dispersed in aluminum. Basically, fuel cores are made by: (1) blending commercial type 101 aluminum powder* with U_3O_8 powder at room temperature, and (2) isostatically compacting the mixture to form cylindrical billet cores. These pre-forms are then welded into a type 8001 aluminum (an aluminum-nickel alloy) billet, degassed under vacuum at an elevated temperature, and then coextruded into tubes. Since these fuels contain a ceramic actinide core (U_3O_8) dispersed in a metal matrix (aluminum), they are also referred to as cermet fuels.^{1,5}

The phase assemblage of U_3O_8 -Al cermet fuels constitutes a non-equilibrium mixture which could, under certain conditions, undergo a metallothermic oxidation-reduction reaction analogous to, but not as exothermic as, the classical thermite (iron oxide-aluminum) reaction.^{1-3,5-10} This type reaction has long been known, but the published ignition temperature ($> 850^\circ C$) of the U_3O_8 -Al reaction is far above the melting point ($660^\circ C$) of the aluminum fuel tubes. Potential concerns with U_3O_8 -Al cermet fuel, therefore, arise not during the low-temperature, normal operation of a nuclear reactor, but under severe accident conditions. If there were a mechanism to reduce the ignition temperature of the U_3O_8 -Al metallothermic reaction to below the temperature the fuel element reached during a temperature transient, then localized ignition of the reaction may introduce a chemical heat source within the nuclear reactor core that could possibly propagate and involve a significant portion of a single fuel assembly. If radial propagation were possible, a significant portion of the nuclear reactor core could become involved.

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This accident scenario, however, is based solely on thermodynamic models and predictions. This scenario also does not take into account chemical changes that occur within the cermet fuel during elevated temperature manufacturing processes. It is important to note that thermodynamic predictions in no way reflect either the kinetics of, or the ignition temperature of, the reactions. Although chemical thermodynamics predict whether a reaction is possible, many other factors contribute to the actual occurrence or non-occurrence of a given reaction. The presence of other phases in a given system may ignite the reaction at a lower temperature, catalyze the reaction at a set temperature, inhibit the propagation of the reaction, or prevent the reaction from proceeding at all.

Prior experience¹¹⁻¹³ at SRP has amply demonstrated that gross concentrations of impurities could initiate solid-state aluminothermic reactions at temperatures $< 400^{\circ}\text{C}$. As the normal Al_2O_3 layer at the interface between the oxidant and the aluminum metal inhibits reaction, a fluxing mechanism can be proposed. Once the integrity of the Al_2O_3 layer is lost via dissolution in the flux, the aluminothermic reaction can proceed. Series of differential thermal analysis studies were undertaken to test a fluxing hypothesis. This hypothesis would be stated:

"A low level of impurities within powder metallurgically prepared $\text{Al-U}_3\text{O}_8$ compacts could potentially act as a flux to dissolve the protective Al_2O_3 coating on the aluminum powder. This would allow intimate contact of aluminum metal (reductant) and U_3O_8 (oxidant) powders resulting in the initiation of kinetically significant reactions at temperatures below the melting point of aluminum."

The goal of this work is to evaluate this hypothesis and define its practicality versus the application of cermet fuels at Savannah River.

SUMMARY AND CONCLUSIONS

Impurities expected in the proposed SRP cermet fuel caused no measurable effect on either exothermic or endothermic $\text{U}_3\text{O}_8\text{-Al}$ reactions below 800°C . Above 800°C , however, impurities caused minor modifications of the reaction thermograms as determined by differential thermal analysis. In similar experiments with Fe_2O_3 and NiO , major modifications of the exothermic oxidation-reduction reactions were evident when NaCl was added as an impurity. At NaCl concentration of 10 wt %, the $\text{Fe}_2\text{O}_3\text{-Al}$ and NiO-Al oxidation-reduction reaction actually began in the solid state. Although the fluxing hypothesis has significant effects on the ignition point of the Fe_2O_3 and NiO reactions with aluminum, the fluxing hypothesis was shown to have no significant effect on the aluminothermic reaction between aluminum and U_3O_8 .

Differential thermal analysis (DTA) has been used to study the effect of impurities on aluminothermic reactions of commercial type 101 aluminum powder with U_3O_8 powder. No measurable effect on the reaction below 660°C (solid state reactions) were observed during differential thermal analysis of (1) loose blended powders, (2) blended and compressed powders, (3) blended, heated and compressed powders, or (4) blended, compressed, and heated compacts containing less than 50,000 ppm impurities from group IA halide salts and group IIA oxides. The DTA scans were obtained using a N_2 purge gas, a temperature ramp of $20^{\circ}\text{C}/\text{min}$, and a cyclic temperature range of 100°C to 1250°C then back to 100°C . Impurities chosen were those which would be expected to be introduced naturally through the powder metallurgical process and those which would be expected to grow in as fission products. Impurity concentrations were evaluated well beyond concentrations attainable via logical process upset or accident scenarios.

It was determined that impurities (> 5 wt %) of alkali metal chlorides, and alkaline earth oxides, cause minor modifications of the reaction thermograms above 800°C for molten aluminum metal with U_3O_8 . It was also determined that attempts to prepare alkali, alkaline earth, and transition metal uranates under process conditions, via reaction of impurities with U_3O_8 prior to compaction with aluminum powder, also did not affect reactions below 660°C.

In similar experiments, it was determined that NaCl does modify the reactions between aluminum metal and Fe_2O_3 and between aluminum metal and NiO. With increasing NaCl concentrations, the temperature of the initiation of the reactions moves to lower temperatures. At 10 wt % NaCl, the exothermic "thermite" reactions between aluminum and Fe_2O_3 or NiO begin in the solid state at approximately 640°C.

The fluxing hypothesis is shown to have no significant effect on the aluminothermic solid state (< 660°C) reaction between aluminum metal and U_3O_8 . Therefore, the powder metallurgy fuel tubes do not add a significant chemical heat source under transient reactor conditions. (Heat transfer calculations¹⁵ show that the cermet core temperatures greater than 300°C cannot be obtained because of the high core thermal conductivity of the aluminum so long as the reactor is flooded with water.) Sufficient energy input from other sources would be required to elevate the temperature well above the melting point of the fuel cladding prior to initiation of the Al- U_3O_8 reaction. Therefore, significant core damage (melting) would have already occurred prior to the Al- U_3O_8 "thermite" reaction beginning.

An added level of protection from tramp impurities affecting the reactor heat load occurs in the fuel fabrication process. Thrice during the fabrication process, the cermet cores are heated to above the maximum reactor fuel temperatures. Prior to extrusion, the cores are outgassed for hours at a temperature in excess of 500°C. Just prior to extrusion, the cermet cores are again heated to greater than 400°C, loaded into the extrusion press and extruded. After extrusion, the tubes are again heated to greater than 400°C during quality control testing. It is, therefore, probable that if a metallothermic reaction were to occur in the cermet fuel, the reactions would take place during the fabrication process and not in the reactor.

BACKGROUND

Concerns

In the aftermath of the April 1986 reactor incident at the Chernobyl Nuclear Power Station in the Soviet Union, SRP and SRL placed an even greater emphasis on its ongoing reactor safety studies. This expanded emphasis included not only present, but also future reactor operations.

If heated to a sufficiently high temperature, the Al- U_3O_8 cermet fuel is susceptible to exothermic reactions. In an Low Temperature Heavy Water (LTHW) reactor, the primary concern becomes the temperature at which the exothermic reaction begins, and can that temperature be reached either under normal reactor operations or under accident conditions. If during a reactor transient the fuel meat can be heated to a temperature sufficient to ignite the reaction, then an energy release could possibly result from the oxidation of aluminum and the corresponding reduction of the U_3O_8 . These reactions have been well studied and are typically known to ignite at 875 to 1000°C. This, of course, is well above the melting point of aluminum (~ 660°C for aluminum alloys used in reactor operations; 660.2°C for pure aluminum).

Although highly electropositive, aluminum is, nevertheless, resistant to oxidation¹⁴ because of the hard, tough film of oxide that quickly forms on the metal's surface. It is, therefore, postulated that the onset of reaction between blended powders of aluminum and less electropositive metal oxides (e.g. Fe_2O_3 , Fe_3O_4 , NiO , Cr_2O_3 , UO_3 , U_3O_8) is inhibited by the presence of this adherent Al_2O_3 film at the interface between the aluminum and the metal oxides. It could be argued that above 875°C , the Al_2O_3 film on the surface of molten aluminum droplets begins to lose its effectiveness as a barrier to surface reactions.

Heat transfer calculations¹⁵ have shown that the maximum center line temperature of a cermet fuel tube, even under most severe accident conditions, would not exceed 300°C . Realistically then, for an aluminum-uranium oxide oxidation-reduction reaction to introduce a significant chemical heat flux into the reactor, a mechanism must exist to reduce the ignition temperature of the aluminum-uranium oxide reaction to below the maximum obtainable temperature within the cermet fuel.

It is well known that if the protective effect of the oxide film on aluminum is overcome, rapid oxidation of aluminum, even by water, can occur. The protective coating can be overcome by scratching, by amalgamation, or by hot alkali hydroxides, halogens, and various non-metals. Highly purified aluminum is attacked by HCl containing cupric chloride or by HCl when the aluminum is in contact with platinum if H_2O_2 is added during the dissolution.¹⁴

To formulate a program to answer the above concerns, this report has translated the above concerns into the following questions:

1. Will "impurities" introduced via the normal feedstock used for the cermet fuel tube fabrication lower the ignition point of the $\text{Al}/\text{U}_3\text{O}_8$ reaction?
2. Will "impurities" introduced via the recycle of reject tubes into the feedstock used for fabrication lower the ignition point of the $\text{Al}/\text{U}_3\text{O}_8$ reaction?
3. Will "impurities" introduced by the fissioning process lower the ignition point of the $\text{Al}/\text{U}_3\text{O}_8$ reaction?
4. If the "impurities" introduced prior to fuel irradiation lower the ignition point of the $\text{Al}/\text{U}_3\text{O}_8$ reaction, will these reactions occur during the fabrication and acceptance testing operations, or will the reactions occur in the reactor during a reactor transient situation?
5. Does the reaction release enough energy to affect reactor safety in the event of a thermal transient?

Prior Work on $\text{Al}-\text{U}_3\text{O}_8$ Reactions

Cermet nuclear fuels and targets were first used in research and test reactors¹⁶ and later in production reactors at Savannah River.^{5,11} Cermet elements¹⁶ have cores that contain ceramic actinide (UO_2 , U_3O_8 , PuO_2 , or NpO_2) particles that are uniformly dispersed in a metallic matrix such as aluminum, stainless steel, or zirconium alloys. These fuel cores are then surrounded by a continuous metal phase which acts as a fission product release barrier. The cermet concept incorporates the desirable properties of both the pure ceramic and the metallic materials without retaining the worst of their poorer qualities. The ceramics offer excellent stability under neutron irradiation in comparison to many actinide alloys, yet are too mechanically unstable to be used alone in many types of fuels and targets. Using powder metallurgy⁵ techniques, these ceramic

powders can be first blended with metal powders and then compressed to yield pre-forms for further fabrication. These pre-forms can then be clad with a suitable metal for further fabrication operations such as extrusion or rolling. The metallic powder provides ductility, ease of fabrication, high thermal conductivity; the metal cladding then provides a suitable barrier to contain both solid and gaseous radioactive fission products.

Research efforts expended at Oak Ridge National Laboratory (ORNL), Argonne National Laboratory (ANL), and Savannah River Laboratory (SRL) during the 1950's, 1960's 1970's and 1980's have yielded various readily fabricated and acceptably stable cermet forms. Plate-type^{1,16} fuel elements have found application in the Puerto Rico Nuclear Center Reactor (circa 1960), the High Flux Isotope Reactor (beginning about 1965), the High Flux Beam Reactor, the National Bureau of Standards Reactor, and the Oak Ridge Research Reactor. Tubular-type cermet target elements of NpO_2 and aluminum have been used at SRP for the production of ^{238}Pu since the late 1960's; cermet target elements of PuO_2 and aluminum have been used for production of heavy elements (^{242}Pu , ^{243}Am , and ^{244}Cm) since the 1970's.

It was recognized in the 1950's that an assemblage of aluminum metal-actinide oxides constituted a non-equilibrium mixture, and that a cermet fuel or target could ultimately tend to change phases with potentially dangerous consequences. In the aluminum- U_3O_8 system, six ideal reactions are possible, neglecting the formation of nonstoichiometric compounds. These possible reactions are:

Major features of reactions between aluminum and U_3O_8 were delineated by Fleming and coworkers,^{7,8} Baker and Bingle,⁹ Ivins and Testa,¹⁰ and by Pasto, Copeland, and Martin.¹ Other investigations in this area were performed by Gray and Kerrigan,¹¹⁻¹³ Rolig,^{10,17} and by Ondracek and coworkers.¹⁸⁻¹⁹ Differential thermal analysis (DTA) of compacted U_3O_8 -aluminum metal powders¹ have shown that:

- On heating, U_3O_8 -Al mixtures exhibit several distinct thermal energy releases^{1,11-13} or absorptions. These include an exotherm between 600°C (973°K) and the melting point of aluminum, an endotherm on melting of aluminum at about 660°C (933°K), an exotherm at approximately 900°C (1173°K), and one or two more exotherms at $> 1200^\circ\text{C}$ (1473°K).
- Heats of reaction for U_3O_8 -Al compositions have been experimentally determined to be much lower than values described in the literature.¹ The heat evolved in the exothermic reaction of compacts containing 50 wt % Al-50 wt % U_3O_8 at about 900°C (1173°K) is about the same as the heat absorbed by the melting of aluminum. The heat absorbed by aluminum upon melting

is 95 cal/g; the heat of the Al-U₃O₈ reaction has been experimentally determined to vary from about 95 to about 125 cal/g of U₃O₈ reacted.

Several research teams have, however, reported time-dependent reactions between uranium oxide powders and aluminum powder during high-temperature fabrication processes. Waugh^{2,3} reported the reaction

reached 90 to 100% completion in 10 hours at 600°C (973°K) in 52 wt % UO₂-Al fuel plates. Beaver and Cunningham²⁰ reported the U₃O₈-Al reaction was much slower; 3000 hours were required for complete reaction at 600°C (973°K). There is also evidence that during normal fabrication procedures, the outside surfaces of the U₃O₈ particle is converted to U₄O₉.

The worst behavior¹ noted as results of these time-dependent reactions have been fuel plate swelling and warpage. This was a concern mainly to fabricators who had to braze reactor fuel elements at temperatures up to about 600°C. The advent of roll swaging for plates and extrusion for tubes solved the fabrication problems.

Manufacturing of Aluminum-Uranium Oxide Fuel Tubes

The general manufacturing process⁵ proposed by SRL for preparing oxide powder metallurgical fuel tubes is shown schematically in Figure 1. First, uranium oxide and commercial type 101 aluminum powders are blended and compacted (~ 80% of theoretical density) into billet cores using cold isostatic compaction. The compacted powder cores are placed into inner and outer sheaths of Al-8001 aluminum alloy. Plugs made of an Al-5052 aluminum alloy containing 2.8% Mg (for hardness) are used at the front and rear of the billet. See Table 1 for specifications of the three alloys of aluminum used.

After outgassing and just prior to extrusion, the billets are preheated to near the extrusion temperature. After extrusion, the tubes are cleaned and cold drawn to straighten. The tubes are blister tested at elevated temperature prior to the final quality control inspections. Those tubes passing inspection are delivered to the reactors; those not passing inspection are recycled.

Reject Tube Recycle

Based upon past experience with making fuel tubes from uranium-aluminum alloy cores, a reject rate of 15-20% is expected. With the PM process, it is proposed that the reject tubes be recycled by dissolving the aluminum in a solution of sodium hydroxide and sodium nitrate. The remaining solids (primarily uranium oxide) would then be separated from the solution by filtering. After washing, drying, and then baking, the uranium oxide is recycled as blendstock to begin fabrication of another fuel tube.

For each kilogram of aluminum to be dissolved, an aqueous solution consisting of 3.4 kg sodium nitrate and sufficient sodium hydroxide to yield a NaOH/Al mole ratio of 1.65 must be used. The NaNO₃ is added so that ammonia (NH₃) is formed instead of hydrogen (H₂) since

Figure 1. PM Fuel Tube Fabrication Process at SRS

Table 1. Chemical Compositions of Aluminum Alloys Used in Fuel Tubes

<u>Wt %</u>	<u>Aluminum Alloy Designation</u>		
	<u>101</u>	<u>8001</u>	<u>5052</u>
Al ₂ O ₃	.6	-	-
Fe	.15-.25	.45-.7	Fe + Si
Si	.07-.15	.17	.45
Ni	-	.9-1.3	-
Cu	-	.25	.10
Mn	-	-	.10
Mg	-	-	2.8
Cr	-	-	.15-.35
Zn	-	-	.10
Al	99.2	Balance	Balance

the lower flammability limit for NH₃ is higher than it is for H₂. The caustic to aluminum ratio is the minimum required to redissolve and maintain the hydrated aluminum hydroxide in solution. The theoretical chemical equations for dissolving aluminum in NaOH in the presence of NaNO₃ are as follows:

It is estimated that the reaction goes 80% by equation 8 and 20% by equation 9. The empirical equation has been found to be:

Most of the impurities in the aluminum alloys used do not dissolve in caustic, but precipitate as slimy metal hydroxides which are difficult to filter. All these impurities which do not dissolve (either in the caustic dissolution or the subsequent wash steps), of course, remain in the oxide product and end up in another fuel tube.

Impurities and Their Sources

Impurities in the powder metallurgy Al-U₃O₈ fuel cores can arise from the following sources:

1. Impurities in the type 101 aluminum powder.
2. Impurities in the U₃O₈ feedstock.
3. Impurities introduced via the recycle of reject tubes.
4. Impurities introduced via the fissioning process within the reactor core.
5. Process water.

Each source of impurities is discussed below. The actual impurities evaluated are included in Table 7.

Impurities in Type 101 Aluminum Powder

The physical properties, typical chemical analysis, and the impurity specifications for commercially available type 101 aluminum powder are given in Table 2. The major and only significant impurities are Al₂O₃, iron, and silicon, minor impurities include gallium, zinc, vanadium, magnesium, and sodium.

Table 2. Properties of Aluminum 101 Powder

Physical Properties

- Density
 - Apparent 1.1 g/cc
 - Tapped 1.5 g/cc
- Average Particle Diameter (Fisher Sub-Sieve Sizer) 17-24 microns
- Surface Area 0.15-0.25 M²/g
- Screen Analysis, Percent

<u>Mesh</u>	<u>Typical Range</u>	<u>Specification for Shipment</u>	
		<u>Min</u>	<u>Max</u>
+100	0-Trace		0.2
-100+200	0-5		
-200+325	10-25		
-325	75-10	5	90

- Chemical Analysis (Specifications)

	<u>Typical</u>	<u>Max Limit</u>
Al	99.20	
Al ₂ O ₃	0.60	
Fe	0.15	0.25
Si	0.07	0.15
Other Metallics, Each	0.01	0.03
Other Metallics, Total	-	0.15

Table 2. Properties of Aluminum 101 Powder, (contd)

- **Chemical Analysis (Impurities)**

<u>Impurities</u>	<u>Typical Range, ppm</u>
Gallium	30-50
Zinc	100
Copper	< 10
Nickel	< 10
Iron	500-600
Manganese	< 10
Chromium	< 10
Vanadium	10-60
Calcium	< 10
Potassium	< 10
Chlorine	< 20
Sulphur	< 10
Phosphorus	< 1
Silicon	100
Magnesium	20-40
Sodium	10-20
Fluorine	< 5
Boron	< 1

Impurities in U₃O₈ Feedstock

As facilities for onsite uranium recycle are yet to be built, analysis of representative samples from the onsite plant is, at present, impractical. Various products prepared under simulated conditions and from offsite sources are given in Table 3. Also included in this table is the plant essential material (EM) specification for the U₃O₈ powder. Note that the major expected impurities are iron, nickel, and silicon, minor impurities are copper, magnesium, and calcium.

Impurities Introduced via Recycle of Reject Tubes

The procedure for recycle of reject tubes was summarized above. Samples of wet, dried, and baked uranium oxide product for recycle have been analyzed via x-ray diffraction. Results showed the material was mainly U₄O₉ before and after drying, and mainly U₃O₈ after baking when the cake was washed with water to remove the dissolver solution. Minor products after baking were Na₂U₂O₇ and U₄O₉ on occasion.

When the cake was not washed, the product after heating was mainly Na₂U₂O₇, so it is important to wash the cake thoroughly. Energy dispersive spectroscopy (EDS) results showed that there were also trace amounts of aluminum and nickel in the baked product. The magnesium in the end sections has been shown to precipitate a flocculent material which x-ray diffraction has shown to be Mg₆Al₂CO₃(OH)₁₆·4H₂O. Other materials which are possible at the trace level include impurities normally present in the NaOH and NaNO₃ bulk chemicals. The predominant impurity here is NaCl.

The presence of predominantly U₄O₉ in the recycled but unbaked uranium oxide product shows that a slow reduction of U₃O₈ occurs during the three heat cycles experienced during the fabrication process. This slow reaction,

is apparently, the first step in the slow time-dependent reactions reported by Waugh.^{2,3} In the normal fabrication operations, the temperature cycles are a lower temperature (< 500°C) and for less time than reported by Waugh^{2,3} for complete reduction to U(O) and conversion (600°C for 10 hours) to the intermetallic UAl₄.

Impurities Introduced via Fission

Cermet fuel coupons prepared from typical SRP U₃O₈ materials have been irradiated and the fission product inventory determined. The isotopic content was then back-calculated to 0.0 days, indicating the inventory at reactor shutdown. The isotopic contents were then summed to give the summary of elemental composition given in Table 4.

Summary of Impurities

The impurities expected to be contained in the powder metallurgy tubes and their expected source and chemical forms are summarized in Table 5.

Table 3. Chemical Comparison of Uranium Oxide Products, parts per million

Element	Standard U ₃ O ₈	Bio-Rex 70*	Dowex 50W-X8*	AG-MP-50 ^a	Oak Ridge U ₃ O ₈	E. M. Specs ^b
Al	5.8	5.8	5.8	5.8	2.3	
Cr	1.3	1.3	4.3	1.3	20	
Cu	1.7	5.2	< 1	1.7	< 1	50
Fe	20	20	60	60	73	250
Mg	< 1	3.0	< 1	3.0	1.7	75
Ni	12	4	12	4	6	250
N	265	—	15	11	992	
P	5	5	17	5	< 100	
K	6.1	61	6.1	6.1	—	
Si	10	30	10	10	7	300
Na	11	99	11	3.3	2.3	25
Zn	10	1.6	1.6	1.6	< 10	
As	—	—	—	—	< 10	
Sb	< 3	< 3	< 3	< 3	< 2	
Ba	< 6	< 6	< 6	< 6	—	
Be	—	—	—	—	< 0.1	30
Bi	< 4	< 4	< 4	< 4	< 1	
B	< 1	< 1	< 1	< 1	< 0.1	10
Cd	< 1	< 1	< 1	< 1	< 0.1	10
Ca	< 8	< 8	< 8	< 8	8.3	50
Co	< 3	< 3	< 3	< 3	< 1	10
Ga	—	—	—	—	< 1	
Ge	—	—	—	—	< 1	
Au	—	—	—	—	< 1	
In	< 1	< 1	< 1	< 1	—	
Pb	< 5	< 5	< 5	< 5	< 5	
Li	—	—	—	—	< 0.2	10
Mn	< 1	< 1	< 1	< 1	< 1	35
Mo	< 7	< 7	< 7	< 7	< 10	
Nb	—	—	—	—	< 10	
Pd	—	—	—	—	< 1	
Ag	< 1	< 1	< 1	< 1	—	
Sr	< 5	< 5	< 5	< 5	< 20	
Sn	< 5	< 5	< 5	< 5	< 10	
Ti	—	—	—	—	< 4	
W	< 5	< 5	< 5	< 5	< 100	
V	< 2	< 2	< 2	< 2	< 1	
Relative						
Cl	1	1	1	1	—	
F	1	1	3	1	—	
S	30	3	1	1	—	

^a U₃O₈ prepared by loading the specified resin and then calcining.

^b Plant essential materials specification.

Table 4. Typical Elemental Content at Reactor Shutdown (units are grams element/gram-core)

Element	Content	Element	Content
H	2.1E-07	Cs	9.7E-03
He	4.3E-06	Ba	5.3E-03
Li	2.7E-09	La	4.9E-03
O	9.8E-02	Ce	1.3E-02
Al	4.3E-01	Pr	4.0E-03
Co	1.1E-18	Nd	1.3E-02
Ni	1.2E-15	Pm	9.2E-04
Cu	1.8E-13	Sm	2.1E-03
Zn	1.4E-10	Eu	3.0E-04
Ga	1.2E-10	Gd	5.0E-05
Ge	1.7E-06	Tb	1.1E-06
As	5.1E-07	Dy	2.3E-07
Se	8.6E-05	Ho	7.4E-09
Br	9.2E-05	Er	8.2E-10
Kr	1.7E-03	Th	3.6E-09
Rb	1.6E-02	Pu	1.1E-11
Sr	5.1E-03	U	5.2E-01
Y	2.5E-03	Np	6.6E-03
Zr	1.6E-02	Pu	3.6E-03
Nb	5.9E-04		
Mo	1.1E-02		
Tc	3.2E-03		
Ru	6.8E-03		
Rh	1.2E-03		
Pd	1.0E-03		
Ag	2.5E-05		
Cd	1.5E-05		
In	4.6E-06		
Sn	8.9E-05		
Sb	3.5E-05		
Te	1.4E-03		
I	6.3E-04		
Xe	2.0E-02		

Table 5. Summary of Major Impurities and Their Expected Chemical Forms

<u>Element</u>	<u>Source</u>	<u>Probable Chemical Forms</u>
Na	Recycle	NaCl, NaOH, $\text{Na}_2\text{U}_2\text{O}_7$
Cs	Fission Product	Cs_2O , CsI
I	Fission Product	CsI
Mg	Recycle	MgO
Ca	Process Water	CaO
Ba	Fission Product	BaO, BaI_2 ?
Sr	Fission Product	SrO , SrI_2 ?
Cr	Corrosion	Cr_2O_3
Fe	Corrosion	Fe_2O_3 , $\text{Fe}_2(\text{SO}_4)_3$
Ni	Corrosion, Recycle	NiO, NiSO_4
Cu	Process Water	CuO
Al	Aluminum	Al_2O_3

EXPERIMENTAL PROCEDURE

Preparation of Cermet Samples

Cermet pellets were prepared using a mortar and pestle to blend and grind together weighted amounts of U_3O_8 , type 101 aluminum powder, and the added impurity. Weighted lots were then pressed to 1200 pounds force ($> 30,000$ psi) in a 3/16-inch diameter die (0.027 square inch). For the differential thermal analysis studies, the pellets were broken and segments used to fill the Al_2O_3 /platinum DTA sample cups.

To aid in positive peak identification, pellets were also prepared with 50 wt % U_3O_8 -50 wt % Al, 100 wt % Al, and 50 wt % Al-50 wt % impurity.

To better understand and compare Al- U_3O_8 reactions with the classical thermite reactions, cermets were also prepared using Al- Fe_2O_3 , and Al-NiO. Impurities were added and pellets pressed as given above for the U_3O_8 -Al cermet pellets. For the differential thermal analysis studies, these pellets were also broken and segments used to fill the platinum DTA sample cups.

Preparation of Uranates under Simulated Process Conditions

Two methods were used to prepare possible uranates under simulated process conditions. The first method used 50 wt % mixtures of possible impurity compounds and U_3O_8 powder. These were ground with a mortar and pestle and then heated to $950^\circ C$ for 16 hours. Upon determination of feasible uranates, stoichiometric mixtures of the impurity compound and U_3O_8 powders were ground with a mortar and pestle and heated for 16 hours at $950^\circ C$.

Cermet pellets of metal uranate-aluminum powder were also prepared, both with and without added impurities, and differential thermograms were obtained as given above.

Powder Metallurgy Tube Samples

Samples were also removed from full-scale and small-scale powder metallurgy (PM) prepared fuel tubes. As these were already blended, pressed, and extruded, further sample preparation was not necessary.

Instrumental

Differential thermal analyses (DTA) were carried out in a dynamic nitrogen atmosphere on a Du Pont 1090 Differential Thermal Analyzer (E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware) utilizing the 0 to $1600^\circ C$ DTA head and platinum sample cups. The reference cup was filled with Al_2O_3 . A scan rate of $20^\circ C$ /minute was used throughout the study using a cyclic temperature range of $100^\circ C$ to $1250^\circ C$ to $100^\circ C$. The temperature calibration was cross-checked with tin, zinc, and aluminum samples. The aluminum acted as an internal standard throughout the DTA experiments.

X-ray diffractometry was performed on a 2.5 kW x-ray generator and a vertical goniometer (North American Philips Co., Inc., New York, New York).

DISCUSSION AND INTERPRETATION OF RESULTS

Al-U₃O₈ Reactions

Typical differential thermograms for aluminum and U₃O₈ powders and for an Al-U₃O₈ cermet pellets (50-50 wt %) are shown in Figure 2. In general, the exothermic and endothermic reactions detected are easily explained by referring to previously published results.^{1-3,5-13,16-28}

The cyclic thermogram for aluminum metal shows the melting endotherm and the solidification exotherm at about 660°C. Since aluminum is a major component of all the compacts, the melting endotherm acts as an internal temperature standard for all thermograms of each of the compacts. The theoretical heat of this transition is 2.57 kcal/g-atom of aluminum (or approximately 95 cal/g of aluminum). The area within the melting peak (endotherm), therefore, serves as a general internal standard for the heats of other reactions occurring throughout the differential thermograms. The area under the solidification peak (exotherm) serves to indicate how much aluminum was consumed via reaction with U₃O₈ to yield Al₂O₃ and the UAl_n (n = 0 to 4) intermetallics during the higher temperature reactions.¹¹⁻¹³

The second thermogram in Figure 2 is for the U₃O₈ powder. This sample was removed from the sample lot of U₃O₈ powder used throughout this set of experiments. The only significant feature noted in this thermogram is the loss of sorbed water in the region of 100-200°C.^{11,12} Using both DTA and a hot stage x-ray diffractometer, Notz²¹ was able to show that orthorhombic α-U₃O₈ undergoes a second-order transition (no detectable heat of transition) to hexagonal U₃O₈. This transition is complete at about 250°C. There is also a small endotherm at approximately 600°C. This is evidently the result of an impurity transition, as yet unidentified.

The third thermogram in Figure 2 is for an Al- U₃O₈ compact. Prior to about 300°C, the small endothermic transitions noted in the Al- U₃O₈ pellet and the loose U₃O₈ powders are the same. These loss-of-water transitions are slower in the pellets due to longer diffusion paths necessary to remove sorbed water from the compacted pellets than from the loose powder.

The exothermic reaction beginning at about 600°C has been studied by Fleming and Johnson,^{6,7} Handwerk, et al.,²⁶ Gibson and Shupe,²⁷ Vogel, et al.,²⁸ by Gray and Kerrigan,¹¹⁻¹³ and by Pasto, Copeland, and Martin.¹ By varying the aluminum to U₃O₈ ratio and the static heating time at 600°C, Fleming and Johnson⁶⁻⁷ were able to show by x-ray diffraction that the products UO₂ and Al₂O₃ were formed. They attributed these products to the reaction

Handwerk, et al.,²⁶ suggest this reaction is incomplete and postulated the formation of an aluminum oxide barrier around the reacting U₃O₈ particles. Gray and Kerrigan¹¹⁻¹³ found x-ray diffraction evidence for UO₂ and U₃O₈, in agreement with Handwerk, et al.,²⁶ and Pasto, et al.¹ Other published data suggests that UAl₄ is also formed in this reaction.

Figure 2. DTA for Aluminum Powder, U₃O₈ Powder, and Al-U₃O₈ Compact

Pasto, Copeland, and Martin¹ attempted to define the phases present by heating specimens in the DTA to temperatures of about 750°C followed by rapid cooling and analysis by XRD. This method was not sensitive enough to detect any Al₂O₃ or UO₂ products. The method would have detected any product comprising 5 to 10 wt % of the mix. These results support other investigators who contend that this exotherm is the result of a surface reaction phenomena, resulting in only a thin layer of reaction product phase.

The literature explanations for this 600°C exotherm are not very satisfying. For one, the area of the peak is highly variable from sample to sample. Compare the curves in Figure 3. The first thermogram is the identical curve shown in Figure 2.

The second thermogram was obtained from a pellet prepared from other lots of both U₃O₈ and type 101 aluminum powder. The peak at about 600°C is much more pronounced in the second thermogram. Regardless of the explanation for the exothermic transition at about 600°C, the reactions were quenched when the aluminum melts at 660°C, as shown by the endothermic peak.

A variety of workers have also studied the exothermic reduction of U₃O₈ by liquid aluminum. As shown in Figures 2 and 3, these reactions begin about 925 to 975°C. By varying the aluminum to U₃O₈ ratio, Fleming and Johnson^{6,7} suggested that the following reactions occurred:

In agreement with Pasto, Copeland, and Martin,¹ studies at SRL have shown that repeated DTA runs of the blended cermet pellets yield exotherms which vary widely in onset temperature, peak shape, and duration. Also in agreement with Pasto, et al.,¹ it must be concluded that all of the potentially available reaction heat is not released in the observed temperature range of approximately 800 to 1000°C. Pasto, et al.¹ give several possible reasons for this fact:

- A. Heat release rate is a function of heating rate, and faster rates would probably result in larger concentrated heat releases. Up to the 20°C/min rate evaluated in the present test, however, no significant effect is observed.
- B. Reaction rate, and thus heat release, is probably inversely proportional to U₃O₈ particle size, and finer particles than those used could result in larger thermal energy releases.
- C. The heat of reaction calculation of Fleming and Johnson^{6,7} assumed complete reaction, which was not the case in the present experiment.
- D. Fleming and Johnson's^{6,7} data for heats of formation were overestimates, based on the best information available at the time. This is possibly the case if the products were UAl₂ and UAl₃, and UAl₄.

Figure 3. DTA of Al- U_3O_8 Reaction for Two Different Feed Lots of Al and U_3O_8 Powders

- E. Part of the thermite reaction thermal energy release may well be represented in the exotherms occurring at the higher temperatures. These peaks occur at temperatures beyond the range of calibration of our instrument, so estimating the heat evolved was not attempted.
- F. Diffusion-controlled reactions, as these are presumed to be, may simply proceed too slowly to exhibit measurable thermal energy release.

Several of Pasto, et al.¹ possible explanations have been studied further at SRL.

In one study, Peacock⁵ plunged cermet pellets into a 1000°C preheated furnace. The energy released during the U₃O₈-aluminum reaction was estimated from temperature-time graphs, to be about 123 cal/g of U₃O₈-aluminum for 53 wt % U₃O₈ pellets. Pasto, et al.¹ reported an experimental value of 95 cal/g of fuel for 52 wt % U₃O₈ in aluminum. Whereas the heating rate by Pasto, et al. was 20°C/minute, the heating rate in Peacock's⁵ study was approximately 780°C/minute. Once the reaction started, Peacock⁵ estimated the maximum self-heating rate to be about 70°C/second. The faster heating rate does indeed result in larger concentrated heat releases.

Baker, et al.^{9,25} and Peacock⁵ have studied the reaction as a function of the particle size of the U₃O₈ powder. Both of these studies confirm that the reaction rate and heat release are inversely proportional to the U₃O₈ particle size. The fact that increasing the U₃O₈ particle size reduces the rate of reaction and lowers the instantaneous energy release is further evidence that the reaction is a diffusion controlled surface reaction.

In general, less than half the calculated heat of reaction was released during these exotherms—the highest measured release was 123 cal/g of fuel reacted⁵ versus 240 cal/g, as calculated by Fleming and Johnson.^{6,7}

Time-dependent reactions were reported by Waugh^{2,3} (90 to 100% completion in 10 hours at 600°C) and confirmed by extrusion and dissolution experiments at SRL. As reported above, tubes processed through the fabrication operations but rejected for any reason are recycled to reuse the uranium. Selective dissolution of the aluminum matrix leaves a uranium oxide residue which is mainly U₄O₉.

Five of the six reasons suggested by Pasto, et al.¹ have, therefore, been confirmed, as stated above. Due to temperature limitation of the Du Pont 1090 DTA instrument used in the present studies, confirmation of reason E above was not attempted.

It is evident that the reactions proceed via a multi-step process. For rapid reaction, there is first the reduction of the higher oxide to UO₂(s), followed by a further reduction to uranium-aluminum intermetallics (UAl₄). Calculations show that the first step ($\Delta H \approx 230$ kcal/g) in the reduction process is more energetic than the second step ($\Delta H \approx 30$ kcal/g). Therefore, so far as the introduction of a possible chemical heat source to a postulated reactor accident, the first reaction raises more concern. It is also evident that 50% or less of the calculated energy (typically 95 to 125 cal/g U₃O₈) is released unless the reaction temperatures reach the 1300 to 1600°C range. Only in this range do the rapid reactions go to completion, and perhaps release the theoretical 250 cal/g, and result in the formation of the intermetallic compounds UAl_x (x = 2, 3, 4). The slower reactions to form UAl_x require extended time periods at elevated temperatures. The heats of these

slow reactions are thermodynamically of no importance in adding a chemical heat source to a transient reactor temperature excursion.

The reduction of $\text{U}_3\text{O}_8(s)$ by $\text{Al}(l)$ to yield $\text{UO}_2(s)$ is an exothermic reaction which yields 227 calories of heat for every gram of U_3O_8 reacted. This is less than 20% of the energy released in the classical "thermite" reaction (iron oxide reduced to iron metal, Figure 4) which yields over 1200 calories of heat per gram of iron oxide reacted. On a molar basis, the heats of reactions are similar.

Classical Thermite Reactions

It appears reasonable to compare the $\text{Al-U}_3\text{O}_8$ reactions to the classical iron oxide- aluminum metallothermic oxidation-reduction reaction, better known as the "thermite" reaction or Goldschmidt process.²⁹ The principal feature of the Goldschmidt process is the exothermic reaction of aluminum and iron oxide in finely divided form to produce iron, aluminum oxide, and considerable heat. The heat generated by the reaction depends upon the formulation. By varying the formulation, the reaction may be held to a temperature just above the melting point of the metal produced, or the reaction mixture can be formulated such that the peak temperature will exceed 1900 to 2200°C. The formulation may use either Fe_2O_3 or Fe_3O_4 as the iron oxide:

Formulations using Fe_3O_4 as the iron oxide apparently reach the higher temperature ranges.²⁹ No auxiliary heat source is necessary to sustain the reaction as it can be ignited by either a fuse or external heat. A typical fuse may consist of a magnesium ribbon terminated in a barium peroxide-aluminum powder ball in contact with the blended aluminum-iron oxide powders. The Goldschmidt process is flexible enough that it can be used in the making of carbon-free metals and various alloys, including ferrotitanium, nickel-titanium, chromium, ferrochrome, manganese, manganese-copper, and manganese-zinc.²⁹

For comparison, differential thermograms for oxides of iron and nickel are given in Figure 4.

Metallothermic Reaction Modification via Impurities

One of the primary objectives of this study was evaluation of the effect that the presence of tramp impurities would have on the initiation temperature of the $\text{Al-U}_3\text{O}_8$ metallothermic reaction. According to some unpublished work by Powers:³⁰

"For the analogous reaction of Al with Fe_3O_4 , it is believed that the onset of the reaction is inhibited by the presence of an adherent Al_2O_3 film at the interface between the metal and the reactive oxide. Above about 1150°K, it is shown that Al_2O_3 films on Al surface begin to lose their effectiveness as a barrier to surface interactions. The effectiveness of the Al_2O_3 film at preventing reaction is sensitive to impurities. Trace quantities of NaCl will reduce the ignition temperature for the thermite reaction from about 1160°K to the melting point of aluminum, 933°K. There is some suggestion that magnesium will do the same."

Figure 4. Differential Thermograms for Classical Goldschmidt Process Reactions

At least a portion of the concern about aluminothermic reactions arises from the fact that exothermic reactions beginning at about 350°C have been previously identified between aluminum and impurities such as sodium uranates, sodium nitrate, and ammonium salts. These low-temperature reactions can release sufficient energy to initiate the aluminothermic reduction of U_3O_8 . Sufficient energy is released only if the impurities comprise a large fraction of the uranium feed in a uniform blend or in localized areas of a nonuniform blend. These reactions are summarized later in this report.

NaCl as an Impurity

Concern about NaCl as an impurity arose from unpublished work on Fe_3O_4/Al reactions. Powers³⁰ pretreated atomized aluminum powder with aqueous solutions of sodium chloride. The results are given in Table 6.

Boiling the atomized aluminum powder in water presumably increased the thickness of the Al_2O_3 coating which maintained its integrity longer than the coating on the untreated powder. The onset of the reaction was increased from 920°C to 1180°C. With a temperature ramp of 20°C/minute, the treated aluminum powder maintained the integrity of the Al_2O_3 coating for about 13 minutes longer than the untreated powder.³⁰

Comparison of the reaction onset of the untreated aluminum powder with powder treated with cold NaCl solution shows only a 2°C difference in reaction onset. This difference is within experimental noise and is, therefore, statistically insignificant.³⁰

Pretreating the aluminum powder by boiling with 1M NaCl lowers the onset temperature of the Al/Fe_3O_4 reaction by about 185°C. These results suggest that chloride salts can in some fashion reduce the ignition point of the Al/Fe_3O_4 reaction. If the mechanism is the result of the interruption of the Al_2O_3 coating on the atomized aluminum powder, then this mechanism may also lower the ignition of other aluminum-metal oxide reactions.

Differential thermograms for Fe_2O_3-Al cermet pellets doped with various amounts of NaCl are given in Figure 5. In full agreement with the unpublished work of Powers,³⁰ NaCl does indeed modify the Fe_2O_3-Al oxidation-reduction reaction. The initiation temperature is lowered until, at NaCl concentration of 10 wt %, the exothermic reaction actually begins in the solid state near the melting point of aluminum. This reaction occurs in the region where a small exothermic reaction appears for aluminum powder as shown in Figure 2. Unlike the 600-660°C exotherm noted with $Al-U_3O_8$ cermets, the NaCl-fluxed Fe_2O_3-Al reaction is not completely quenched by the melting of aluminum. The reaction does become more energetic after the aluminum has melted.

Differential thermograms for $NiO-Al$ cermet pellets doped with various amounts of NaCl are given in Figure 6. Analogous to the Fe_2O_3-Al cermets, NaCl also modifies the $NiO-Al$ oxidation-reduction reaction. The initiation temperature of the $NiO-Al$ is lowered by the addition of NaCl until the reaction begins near the melting point of aluminum.

For comparison, NaCl was doped into U_3O_8-Al cermets. The resulting differential thermograms are given in Figure 7. Note that there is only slight modification of the high temperature exothermic reaction even when NaCl concentrations of 10 wt % are used. Note that the melting point of NaCl is clearly evident at approximately 800°C in the 10 wt % cermet pellet. Also note that in the production preparation of 50-50 cermet blends of U_3O_8 and aluminum powders, the U_3O_8 powder would have to contain NaCl as an impurity at the 20 wt % level to produce a

Table 6. Effect of NaCl on the Ignition of the $\text{Fe}_3\text{O}_4/\text{Al}$ Reactions

<u>Mixture</u>	<u>Extrapolated Onset of Reaction (°C)</u>
$\text{Fe}_3\text{O}_4 + \text{Al}$	920
$\text{Fe}_3\text{O}_4 + \text{Al}$ (Al boiled in H_2O)	1180
$\text{Fe}_3\text{O}_4 + \text{Al}$ (Al treated with cold NaCl solution)	922
$\text{Fe}_3\text{O}_4 + \text{Al}$ (Al boiled in 1M NaCl solution)	735

Figure 5. Differential Thermograms for Classical Goldschmidt Process Modified by the Addition of NaCl (Fe₂O₃-Al Reactions)

Figure 6. Differential Thermograms for Classical Goldschmidt Process Modified by the Addition of NaCl (NiO-Al Reactions)

Figure 7. Differential Thermograms for $\text{U}_3\text{O}_8\text{-Al}$ "Thermite" Reactions as Modified by the Addition of NaCl

cermet with 10 wt % NaCl. The essential materials specification (Table 3) for sodium in the U_3O_8 feedstock is 25 ppm versus the $> 75,000$ ppm sodium required to give 20 wt % NaCl.

Other Impurities

Various other impurities were doped into the U_3O_8 -Al cermet pellets. Selected thermograms are given in Figures 8 to 11. A summary of onset reaction temperatures for a variety of impurities is given in Table 7. The exotherm at 600 to 625°C wanders around a bit, but changes within the range for using various lots of aluminum powders and U_3O_8 powders. Therefore, there is no significant change in this exotherm.

The first small exotherm above the melting point of aluminum varies from 800 to $\sim 1100^\circ\text{C}$; sometimes, this small exotherm is actually absorbed by the major exotherm.

The major exothermic reaction typically begins a measurable differential temperature in the range of 950 to 1100°C . As a general statement, the greater the concentration of the impurity, the higher the onset temperature of the major exothermic reaction. This is exactly opposite to the hypothesis presented at the beginning of this paper. To add a chemical heat source, it would be necessary to decrease the ignition temperature of the reaction by adding these impurities. Instead of decreasing the ignition temperature of significant exothermic reactions, impurities of either chlorides or oxides, the ignition of the major exothermic reaction is apparently inhibited to some extent.

Thermograms for the U_3O_8 -Al reactions modified with KCl are given in Figure 8. Although the major exotherm which occurs between 900 and 1200°C is modified in shape, there is no apparent lowering of the temperature of ignition below a KCl concentration of at least 5 wt %. There does appear to be a major modification of the peak shape at 5 wt % KCl, but also a much less energetic reaction.

Differential thermograms for alkaline earth oxide modified U_3O_8 -Al reactions are shown in Figure 9. With BaO and SrO, the ignition temperature of the exothermic reaction appears to be delayed until temperatures $> 1000^\circ\text{C}$ are obtained.

Differential thermograms for Fe_2O_3 modified U_3O_8 -Al reactions are shown in Figure 10. Compared to U_3O_8 -Al and Fe_2O_3 -Al reactions, the presence of both oxides appears to delay the ignition of the respective reactions to higher temperatures. The ignition of the Fe_2O_3 -Al reaction is apparently delayed by about 100°C to $> 1000^\circ\text{C}$; the U_3O_8 -Al reaction appears to be delayed to $> 1100^\circ\text{C}$.

As iodine is a major fission product, thermograms of the U_3O_8 -Al reactions modified by the addition of KI were also obtained. These are shown in Figure 11. The peak shape is modified over the KI concentration range of 0.1 wt % to 10.0 wt %, but the ignition temperature is not lowered to less than 900°C .

Figure 8. Differential Thermograms for $\text{U}_3\text{O}_8\text{-Al}$ "Thermite" Reactions as Modified by the Addition of KCl

Figure 9. Differential Thermograms for U_3O_8 -Al "Thermite" Reactions as Modified by the Addition of Alkaline Earth Oxides

Figure 10. Differential Thermograms for U_3O_8 -Al "Thermite" Reactions as Modified by the Addition of Fe_2O_3

Figure 11. Differential Thermograms for $\text{U}_3\text{O}_8\text{-Al}$ "Thermite" Reactions as Modified by the Addition of KI

Table 7. Effect of Impurities on the Exothermic Reactions of 50 wt % U_3O_8 /50 wt % Al Mixtures

<u>Impurity Added</u>	<u>Wt %</u>	<u>Extrapolated Onset of Reaction (°C)</u>		
		<u>Low Temp</u>	<u>First High Temp</u>	<u>Major Exotherm</u>
None		610	> 900	> 900
NaCl	0.1	None	890	1065
	0.5	610	950	950
	1.0	610	950	950
	2.0	600	850	950
	10.0	610	1100	1100
KCl	0.2	None	950	950
	0.5	610	975	975
	1.0	600	1100	1100
	2.0	600	800	1100
	5.0	600	800	1000
CsCl	0.1	610	800	950
	0.2	610	900	1050
	0.5	610	900	900
	1.0	610	950	950
	2.0	610	800	960
	5.0	600	800	960
	10.0	600	810	975
KI	0.1	600	900	1115
	0.5	600	890	1100
	5.0	600	950	1100
Fe_2O_3	0.1	None	800	950
	0.2	600	800	1050
	0.5	None	1000	1125
	1.0	None	1100	1100
	2.0	None	900	1100
	5.0	600	1000	1100
	10.0	600	800	950

Reactions of U_3O_8 with Various Impurities

Sample Preparation

Since the fluxing hypothesis for modification of the Al- U_3O_8 reactions did not appear to be applicable to the Al- U_3O_8 cermets, a second hypothesis was developed. Since the reject tubes will be subjected to selective dissolution of the aluminum with NaOH solution followed by filtration, washing, and then heating of the recovered uranium oxide powder, the possibility of uranate formation was investigated. This hypothesis assumes that sufficient concentrations of uranates are fed into the powder metallurgy recycle feedstock so that the uranates initiate the aluminothermic reactions.

To determine the possibility of uranate formation under simulated process conditions, possible impurities were blended in a 50/50 weight ratio with U_3O_8 powder and then heated at $\sim 950^\circ\text{C}$ for approximately 16 hours. The residual powders were then analyzed by x-ray diffraction to determine the products of reaction.

Since feedstock essential materials specification (Table 3) and process control would reject any U_3O_8 product contaminated with impurities at the 50 wt % level, conditions which more closely simulated actual process conditions were investigated. Stoichiometric amounts of impurities (see Table 8) were blended with U_3O_8 and heated at 950°C for approximately 16 hours (noted that stoichiometric amounts are still much greater than the essential materials specifications would allow). The mixtures were cooled, reground, and heated for an additional 16 hours. The various powders were then divided into lots and treated as follows:

1. One lot was blended with 50 wt % aluminum powder, pellets pressed, and thermograms obtained.
2. The second lot was blended with aluminum powder and 10 wt % of the base impurity, heated for 16 hours at 525°C , pellets pressed, and thermograms obtained.
3. The third lot was blended with aluminum powder and 10 wt % of the base impurity, heated for 16 hours at 525°C , pellets pressed, heated an additional 15 hours at 550°C , and thermograms obtained.
4. The fourth lot was treated as in 3 above, except that the final heating was for 55 hours prior to obtaining the thermogram.
5. An additional impurity, NaCl, was also added to the fourth lot of materials above; the spiked lot was blended with 50 wt % Al powder, pellets pressed, and the thermograms obtained.

Table 8. Reaction of U_3O_8 with Various Impurities

<u>Impurity</u>	<u>Reaction Products</u>
NaCl	$Na_2U_2O_7$
Fe_2O_3	Fe_2O_3, U_3O_8
Cr_2O_3	$Cr_2O_3, U_3O_8, CrUO_4$
NiO	NiO, U_3O_8 , NiU_3O_{10}
$Fe_2(SO_4)_2$	Fe_2O_3, U_3O_8 (Trace Fe_2UO_6 ?)
$NiSO_4$	NiO, U_3O_8
CaO	CaO, U_3O_8 , Ca_2UO_4 , $Ca_2U_2O_7$
MgO	$MgUO_4$, MgO, U_3O_8
CuO	CuO, $CuUO_4$ (CuU_3O_{10} ?)

Results of U_3O_8 -Impurity Reactions

X-ray diffraction identification of the products formed during the 16-hour, 950°C heat cycle of 50 wt % U_3O_8 -50 wt % impurity is given in Table 8. Only three impurities formed significant amounts of the uranates (NaCl, MgO, CaO) under these conditions. The other mixtures remained predominantly a mixture of the reactants. If sufficient amounts of the impurities (NaCl, MgO, CaO) were present in the U_3O_8 feedstocks, then uranate formation during processing may be possible.

Various selected thermograms for the heat-treated compacts are shown in Figures 12 through 16.

These results are in partial agreement with previous work by Gray and Kerrigan.¹¹ Only uranates which crystallize in the pseudo-hexagonal crystal structure (e.g. $Na_2U_2O_7$, $Na_6U_7O_{24}$, $CaUO_4$, and $SrUO_4$) were found to react with aluminum in the solid state. Uranate crystallizing in the orthorhombic crystal system (e.g. α - Na_2UO_4 and $MgUO_4$) and the pseudo-tetragonal crystal system (e.g. $BaUO_4$) did not react with aluminum in the solid state. Gray and Kerrigan¹¹ also determined electron-probe analysis that the reactions between aluminum and the uranates of the pseudo-hexagonal crystal system occurred only at the particle interfaces of the compacted powders. It must be concluded that reaction of impurities with U_3O_8 to yield pseudo-hexagonal uranate under process conditions is insignificant.

Of the materials which could possibly be presented as impurities in the manufacturing process, only sodium compound reacts with U_3O_8 to form pseudohexagonal uranates. Instituting and carrying out a quality control program can control the amount of sodium salts entering the manufacturing operations.

Orthorhombic and pseudo-tetragonal uranates do not add a possible chemical heat source to the reactor fuel tubes since they do not react at low temperatures. The pseudo-hexagonal uranates can be minimized to an insignificant probability level by quality control. Even if the quality control were breached and significant uranates were formed during the processing of the U_3O_8 powders, they would react under the tube fabrication and qualification conditions instead of in the nuclear reactor. Therefore, the pseudo-hexagonal uranates are not a possible chemical heat source to the reactor. Control of sodium impurities, however, is necessary to prevent possible problems in the tube manufacturing operations.

Metallurgical Reactions in Powder Metallurgy Tube Samples

Sample Preparation

As a final check on the overall possibilities that something had been overlooked, powder metallurgy (PM) tubes were prepared, the tubes sectioned, and samples from the cermet fuel meat removed. These were also subjected to differential thermal analysis.

Figure 12. DTA of Alkali Metal Chloride- U_3O_8 Reaction Product Blended with Aluminum

Figure 13. DTA of Alkaline Earth Metal Oxide- U_3O_8 Reaction Product Blended with Aluminum

Figure 14. DTA of Heat-Treated Al-U₃O₈-KCl (45%, 45%, 10%) Mixture

Figure 15. DTA of Heat-Treated Al-U₃O₈-CsCl (45%, 45%, 10%) Mixtures

Figure 16. DTA of Heat-Treated Al-U₃O₈-Cr₂O₃ (45%, 45%, 10%) Mixtures

Results of PM Reactions

A DTA trace for a sample removed from a full-scale PM tube sample is shown in Figure 17. Note that only the endothermic melting peak of aluminum is observed at approximately 660°C. There is an exothermic reaction beginning at about 1000°C but much less energy is released when compared to the energy released for the $\text{U}_3\text{O}_8\text{-Al}$ reaction shown in Figure 2. This is, of course, in keeping with the results found on tube recycle that the uranium oxide powder has been transformed to U_4O_9 during the PM tube manufacturing operations. This is taken as confirmation that within the scope of this study no significant chemical heat source will be added to the reactor via the powder metallurgy fuel tube manufacturing process.

Figure 17. DTA of Core Sample of Extruded U₃O₈-Al Cermet Fuel Tube

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