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Aerosol Characterization from a Simulated HCDA

1979 Annual Report

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SUMMARY

Environmental conditions simulating the HCDA on a reduced scale provided the following information:

Aerosols resulting from the condensation of gaseous constituents without sodium generally comprise small, spherical particles (diameter 0.01 to 0.25 μ m) and branched chain-like structures.

Aerosols resulting from the condensation of gaseous constituents with sodium generally comprise spherical, small (diameter 0.01 to 0.50 μ m) particles, with some branched chain-like structures and some agglomerating particles.

Electron diffraction analyses identified actinide dioxides, the constituents of stainless steel, an oxide of sodium (Na_2O) , sodium uranates $(Na_3UO_4 \text{ and } Na_4UO_5)$, and a sodium plutonate compound (Na_4PuO_5) .

Initial solubility studies indicated that 12.1% of the plutonium-239 dissolved in distilled water when a mixed-oxide (Pu, U) stainless-steel pellet was vaporized with sodium. Reaction products are controlled kinetically during cooling rather than by equilibrium thermodynamics.

1. INTRODUCTION

In support of the Office of Nuclear Regulatory Research, Nuclear Regulatory Commission, Mound Facility has initiated a program to produce and characterize the primary aerosols that could result from a hypothetical core-disruptive accident (HCDA) in a Liquid Metal Fast Breeder Reactor (LMFBR). These tests are being conducted under simulated conditions that can be related to the actual events that would occur under such a critical excursion. The program includes the following:

A feasibility study to determine the possibility of direct acquisition of kinetic information regarding the chemical reactions for the U-Pu-O-Na system in the simulated HCDA environment.

The acquisition of a thermodynamic data base of the possible reactions and species formed from the interactions of the U-Pu-O-Na system.

The simulation of an HCDA event by the laser evaporation technique.

The investigation of the chemical reactions and compounds formed from the short-lived vapor state existing in the HCDA environment.

The assessment of the role of reaction kinetics on both the bubble formation and post-HCDA environment effects on the materials present throughout this accident sequence.

The resulting data are being compared with theoretical and existing analytical data and coordinated with other groups that have developed or are developing models and aerosol data. Large amounts of experimental data exist on the generation and behavior of single-component aerosols, and some limited data exist on aerosols containing both uranium and sodium oxides; but little or no data exist on multicomponent systems containing aerosols generated from (U, Pu)O₂, sodium, and stainless steel produced under HCDA conditions.

Mound has designed and fabricated a system that is capable of incorporating all these materials in a laboratory-scale simulation of an HCDA. The operation of a laboratory-scale simulation will enable the variation of the operating parameters and materials.

2. THEORY

During the most severe hypothetical core-disruptive accidents (HCDA), caused for example by transient overpower (TOP) or loss of flow (LOF), substantial amounts of the reactor fuel, stainless steel cladding, and sodium coolant could be vaporized. The vapor species formed, including PuO, UO, PuO₂, UO₂, UO₃, O, O₂, Na, stainless steel, and the fission products are expected to be contained initially in gas bubbles within the sodium coolant. A temperature gradient within the bubble will exist, initially, from probably greater than 2800°C in the gas phase to about 900°C at the liquid sodium walls of the bubble. As the bubble moves away from the primary heat source, cooling will cause condensation and reactions of various vapor species probably resulting in the formation of an aerosol. In addition, condensation and reactions will occur at the liquid sodium walls of the bubble.

The physical and chemical nature of the aerosol particles is important in predicting the eventual behavior and fate of the aerosol. Physical properties of the aerosol (particle size, density, settling velocity, and coagulation tendencies) are presently being studied, chiefly by vaporization of UO_2 . The chemical nature of the aeroso' particles, which is determined by the chemical species present in the various temperature regimes transited by the aerosol, must be considered because it could affect the physical properties of the aerosol and would definitely influence the subsequent environmental and biological pathways of any aerosol that might escape from the reactor containment structure.

3. EXPERIMENTAL PROCEDURE:

3.1. LASER EVAPORATION

3.1.1. MATERIALS

The radioactive pellets used in the first phase of the study were composed of depleted uranium dioxide, plutonium dioxide, and reactor structural materials mixed to the following compositions (in weight percent):

- 1. 100% UO2
- 2. 100% PuO2
- 3. 80% UO2 20% PuO2
- 4. 75% UO2/PuO2 25% 316 stainless steel
- 5. 75% PuO2 25% 316 stainless steel

The depleted UO₂ was 99.5% pure. The ²³⁹PuO₂ had a plutonium assay of 0.8767 g Pu/g PuO₂ product. The isotopic analysis was 94.0% plutonium-239, 5.8% plutonium-240, 0.30% plutonium-241, and less than 0.05% plutonium-238 and plutonium-242. The 316 stainless steel was Metco 41c powder (45 to 112 μ m size range). The sodium was reagent grade metal which was stored under xylene.

The materials were mixed using a mortar and pestle, charged into a 14-mm-diameter graphite-coated die, and hydraulically pressed at 8.61×10^8 Pa in an argon atmosphere glovebox. The moisture level was less than 1.0 ppm, and the oxygen level was less than 10.0 ppm.

In the second phase of this study, the radioactive pellet compositions were:

- 1. 100% PuO2 Na (Liquid)
- 2. 75% PuO2 25% 316 stainless steel Na (Liquid)
- 3. 75% UO2/PuO2 25% 316 stainless steel Na (Liquid)
- 4. 75% UO2/PuO2 25% 316 stainless steel Na (Liquid) Air

The materials used were the same as those used in the first phase of the study. The materials, after being mixed and charged into the die as described in the first phase of the study, were also pressed at 8.61×10^8 Pa in an argon atmosphere. The moisture and oxygen levels were the same as described in the first phase of the study. Sodium metal was introduced into a depression prepared in the center of the pellets. The pellets were heated to melt the sodium in the depressions just before the laser heating. In the third phase of the study, the radioactive pellet had the following composition:

75% UO2/PuO2 - 25% 316 stainless steel - Na (Liquid)

The materials and method of preparation were the same as those used in the second phase of the study.

3.1.2. METHOD

In all three phases of the study the pellets were heated with a rail laser adapted to use a neodymium glass rod. Figure 1 illustrates the revised static laser heating fixture which was located in an argon atmosphere glovebox. The laser voltage was set at 2.70 keV (24-J output) with a pulse time of 5 msec. The spot diameter was 0.10 cm, and the power density calculated from the spot size was 4.0 MW/cm2. At this power density, a temperature of 10,000 K can be expected in the vapor plume [1]. The energy input to the pellets was approximately 10,000 J/g. The laser beam passed through a 90° directional lens, a lens-prism system, and the guartz top of the static laser fixture, vaporizing a portion of the pellet. Figure 2 illustrates the complete experimental setup used for these studies. In the first two phases of the study, the vaporized portion of the pellet was condensed on both transmission electron microscope (TEM) grids and scanning electron microscope (SEM) stubs as shown in Figure 1. In the third phase, the stub support was removed from the laser heating fixture, and the vaporized portion of the pellet was condensed on glass slides which were suspended under the quartz top.

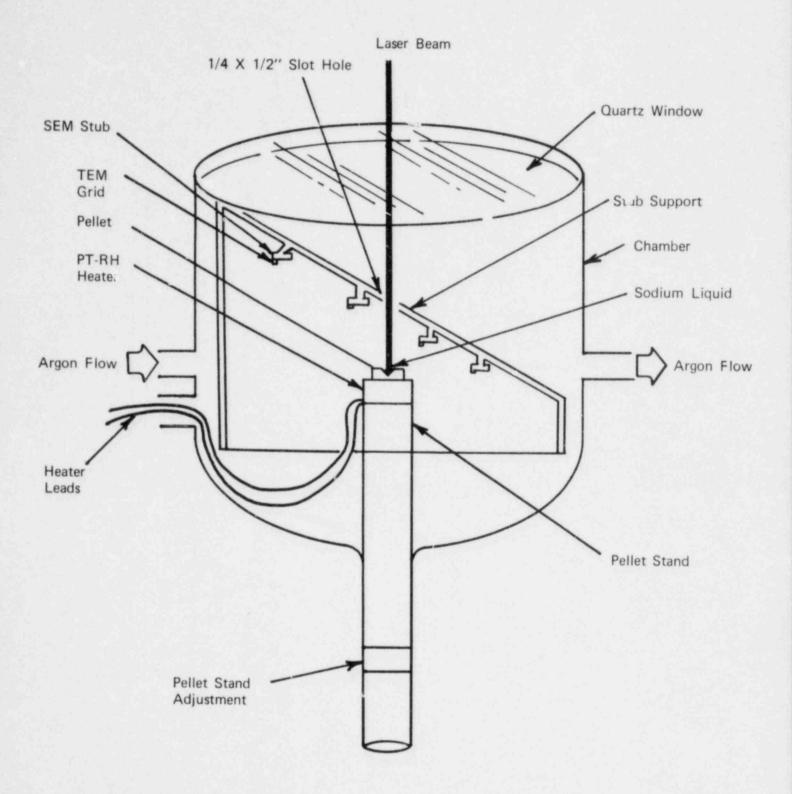
The SEM samples were analyzed for particle size, distribution, and elemental constituents of the particles. The TEM samples were analyzed for particle size, shape, agglomeration (chains), and compound formation (electron diffraction).

The condensate was removed from the glass slides, dissolved in distilled water, and analyzed for plutonium-239 by alpha scintillation counting techniques.

3.1.3. RESULTS

Results for the first two phases of the study were primarily assessed by examining the products via SEM and TEM analyses. The pellet compositions, compounds identified, and aerosol size range data collected from the TEM analyses are summarized in Tables 1 and 2.

The pellets that were laser heated without sodium formed compounds that were not different from the starting components (See Table 1). The compounds identified were UO_2 , PuO_2 , and FeNi. The compound FeNi is a combination product of two of the components of stain-less steel, iron and nickel.



REVISED LASER SYSTEM PERMITTED INERT GAS LASER HEATING

FIGURE 1 - Revised static laser heating system fixture which permits inert-gas laser heating.

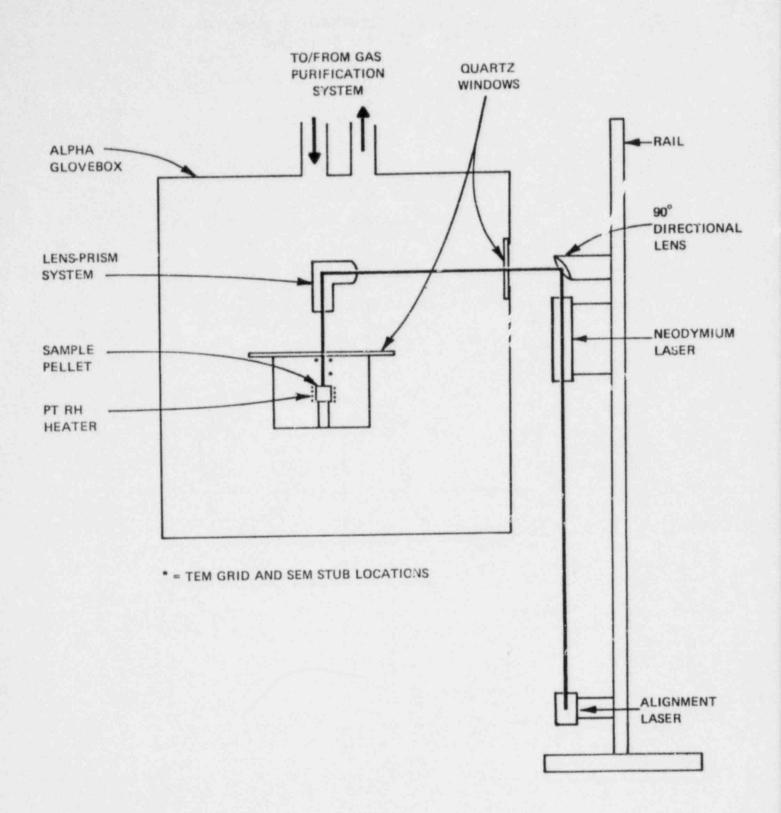


FIGURE 2 - Purified atmosphere (argon) glovebox enabling experiments with plutonium-239 and liquid sodium.

Pellet Number	System	Size (µm)	Major Compounds		
1	UO ₂	0.01 to 0.25	UO ₂		
2	PuO ₂	0.01 to 0.10	PuO ₂		
3	80% UO2-20% PuO2	0.01 to 0.15	UO ₂ , PuO ₂		
4	75% UO2/PuO2-25% SS	0.01 to 0.25	UO_2 , PuO_2 , Fe		
5	75% PuO2-25% SS	0.01 to 0.25	PuO2, FeNi		

Table 1 - AEROSOL SIZES AND COMPOUNDS FORMED IN

The pellets that were heated with formed sodium plutonate (Na_4PuO_5) when PuO_2 was present and sodium uranate (Na_3UO_4) when UO_2 was present. (See Table 2.) Pellet #3 was the closest simulation to the HCDA conditions. The major products from the vaporization of the pellet were the starting components UO_2 , PuO_2 , and iron, a constituent of stainless steel. The minor compounds formed were sodium plutonate (Na_4PuO_5) and sodium uranate (Na_3UO_4) .

Pellet #4 (Table 2) was vaporized in air to simulate the escape of the bubble from the reactor containment to the air environment of the reactor building. The major products formed were UO_2 , U_4O_9 , PuO_2 , Na_2O , and Fe_2O_3 . The minor compound formed was sodium uranate (Na_4UO_5).

Aerosols formed in the third phase of the study were primarily assessed by examining the dissolved products by alpha scintillation counting techniques. The pellet compositions, total mass of plutonium-239 vaporized, total mass of plutonium-239 dissolved in water, and the fraction of plutonium-239 dissolved in water are summarized in Table 3. The initial test indicates that an average of 12.1% of the plutonium-239 dissolved in distilled water when a mixed-oxide, stainless-steel pellet was vaporized with sodium.

3.2. HCDA AEROSOL FORMATION

Figures 3, 4, and 5 are transmission electron photomicrographs of the PuO_2 , UO_2-PuO_2 , UO_2/PuO_2 -SS system condensation aerosols. The particles are spherical, and the diameters range from 0.01 to 0.25 μ m. The photomicrographs show branched chain-like structures that are typical of vaporization condensation aerosols of most metal oxides [1]. These branched chain-like structures from the fields of Figures 4 and 5 are shown in Figures 6 and 7.

Figures 3, 6, and 7 also show some crystalline particles that had not been observed in previous HCDA experiments [2]. The crystalline particles can be attributed to PuO_2 , since they were first

Pellet		Size	Compounds					
Number	System	(µm)	Major	Minor				
1	100% PuO2-Na (Liquid)	0.01 to 0.50	PuO_2 , Na_2O	Na ₄ PuO ₅				
2	75% PuO ₂ -25% SS-Na (Liquid)	0.01 to 0.50	PuO_2 , Fe, Na_2O	Na 4 PuO 5				
3	75% UO2/PuO2-25% SS-Na (Liquid)	0.01 to 0.25	UO_2 , PuO_2 , Fe	Na ₃ UO ₄ , Na ₄ PuO ₅				
4	75% UO_2/PuO_2-25 %-SS-Na (Liquid) (Air)	0.01 to 0.15	UO_2 , U_4O_9 , PuO_2 Fe ₂ O ₃ , Na ₂ O	Na 4 UO 5				

		2 3 9 Pu	mat al	239 Exaction D
		Dissolved	Total 2 3 9 Pu	Fraction Pu Dissolved
Sample Number	System	in H ₂ O (µg)	Vaporized (µg)	in H2O (%)
1	75%UO2/PuO2-25% SS-Na (Liguid)	4.8	24.0	20.0
2	75% UO2/PuO2-25% SS-Na (Liquid)	2.2	23.5	9.4
3	75% UO2/PuO2-25% SS-Na	1.7	24.5	6.9

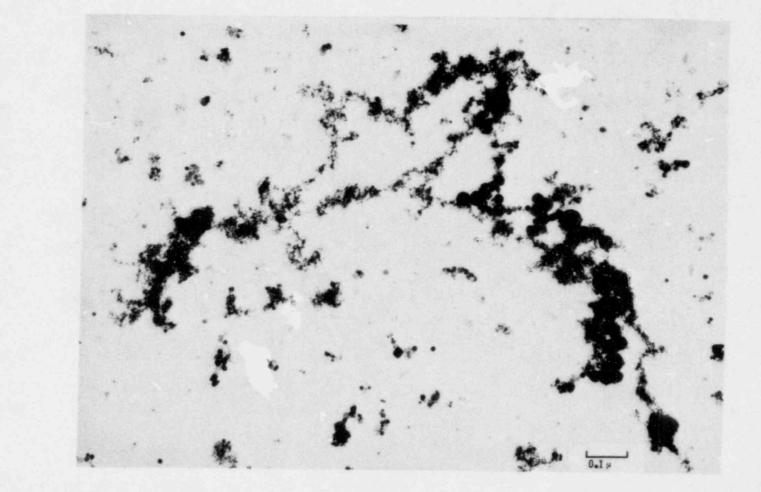
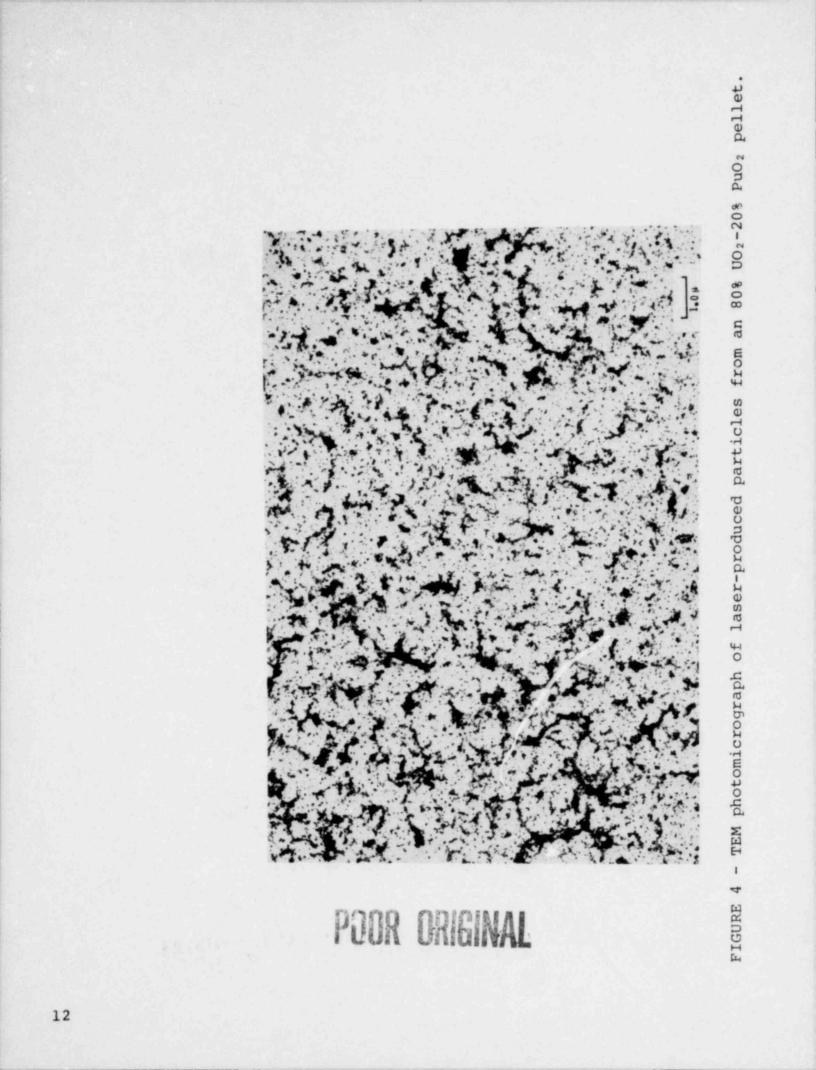
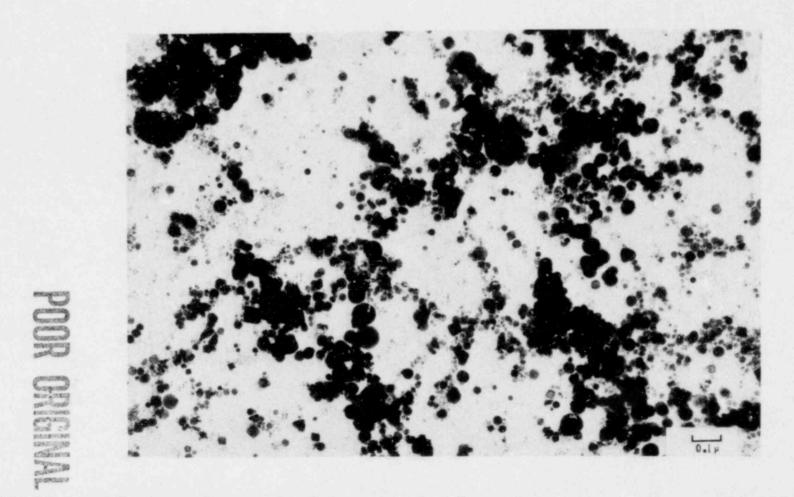
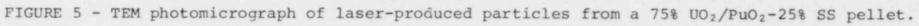


FIGURE 3 - TEM photomicrograph of laser-produced particles from a PuO2 pellet.







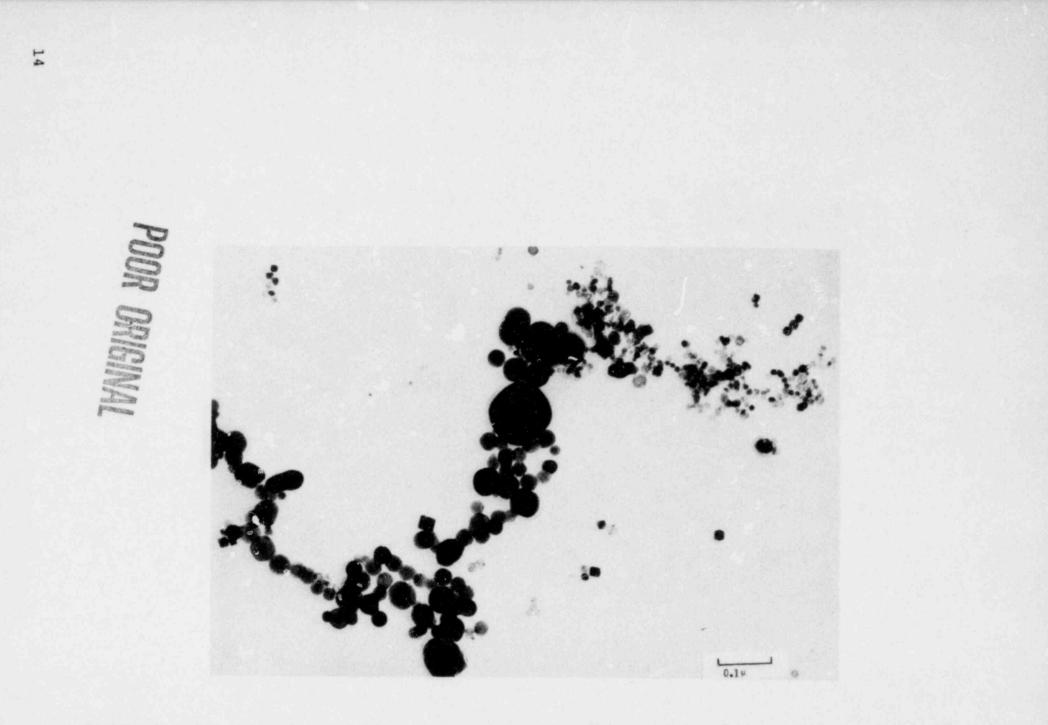


FIGURE 6 - TEM photomicrograph of laser-produced chain particles from an 80% UO_2-20 % PuO_2 pellet.

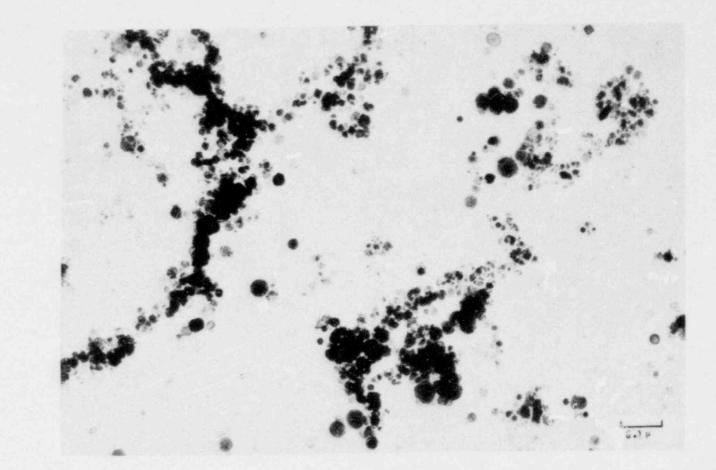


FIGURE 7 - TEM photomicrograph of laser-produced chain particles from a 75% UO2/PuO2-25% SS pellet.

observed in Figure 3 and appear in systems that contain PuO_2 as shown by Figures 6 and 7. The explanation for this phenomenon is not known at this time, although it could be theorized that the lower vaporization point of PuO_2 compared to UO_2 may allow enough time during cooling for the crystalline particles to form.

Electron diffraction patterns were photographed from the particles shown in the fields of Figure 3 through 7. The compounds were discussed in the previous section and are listed in Table 1.

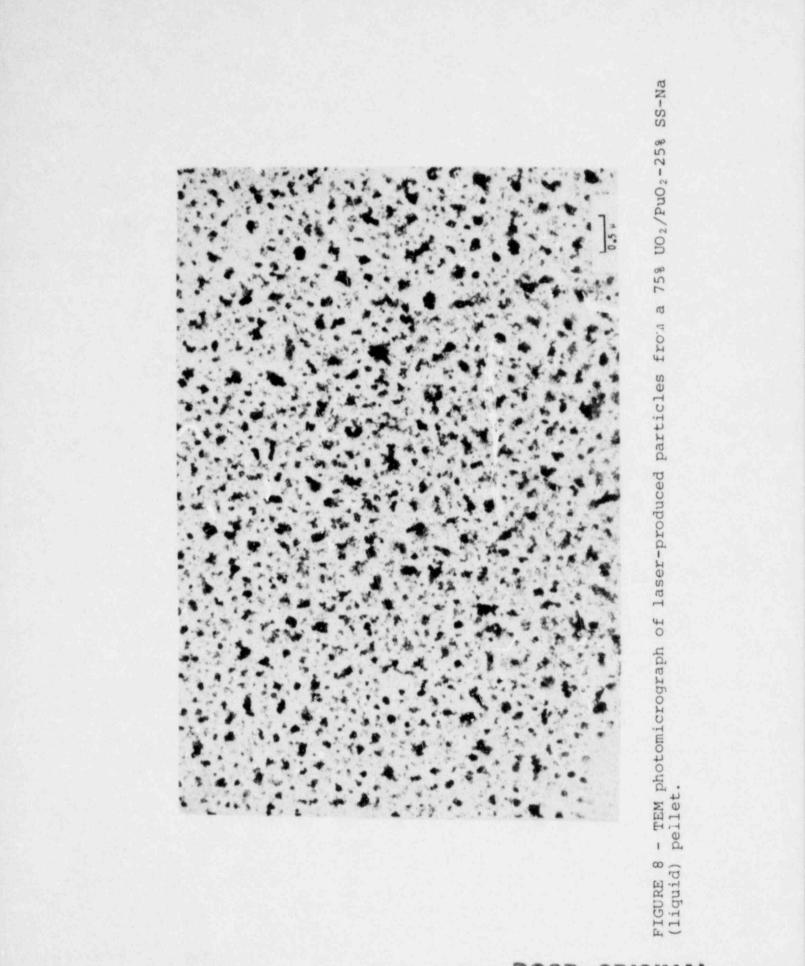
Figures 8 and 9 are transmission electron photomicrographs of the UO_2/PuO_2 -SS-Na (liquid) system condensation aerosols. The particles are spherical and the diameters range from 0.01 to 0.25 μ m. The photomicrographs show branched chain-like structures that are slightly different from those that were vaporized without sodium. There seems to be more agglomeration of the particles, and the particles overlap more in the chain structure as can be seen in Figures 6 and 9. The particles vaporized with sodium seem to have a stronger charge than the particles vaporized without sodium, and thus the charged particles agglomerate more, causing more overlapping and compression of the chain-like structures.

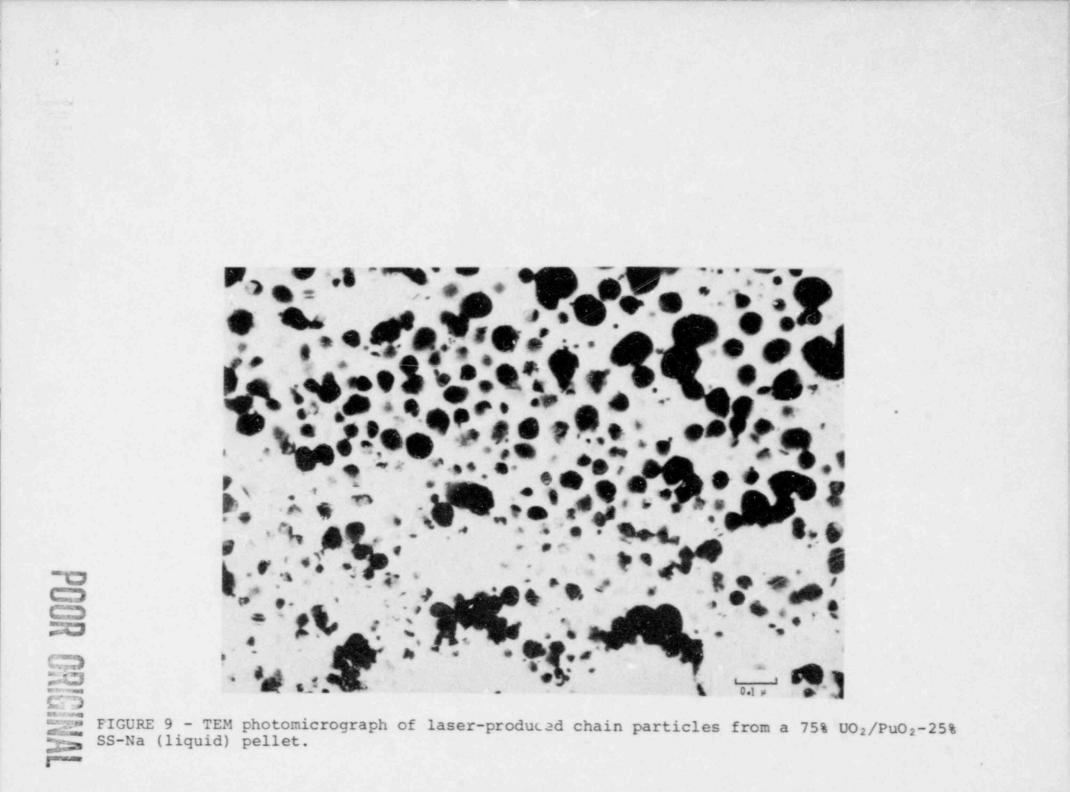
Electron diffraction patterns were photographed from the particles shown in the fields of Figures 8 and 9. The compounds were discussed in the previous section and are listed in Table 2. These compounds and the spherical branched chain-like particles are expected to form as condensation products from an HCDA event.

4. THERMODYNAMIC AND KINETIC CONSIDERATIONS

A thermodynamic assessment of the expected products in an HCDA was previously published [2]. In that work, it was concluded from the free energies of reaction for sodium uranate formation that the distribution of chemical species formed in the hot aerosol was not thermodynamically controlled. The study considered only the system Na-U-O, as data on free energies of formation for the sodium plutonates were not available. A comprehensive computerized literature search indicates that since the issuance of the aforementioned publication no new thermodynamic data on the sodium plutonates have been published. A thermochemical assestment of the possibility of sodium plutonate formation is, therefore, still not possible.

A kinetic assessment of the rate of Na_3MC_4 (M=Pu/U) formation has also been previously published [3]. The conclusion of that work was that Na_3UO_4 formation is entirely possible under the temperaturetime conditions present in both the simulated and real HCDA. Limitations on the applicability of the data to HCDA chemical product predictions were pointed out. These limitations were essentially twofold: first, there was a large temperature extrapolation between measured data and predicted results; second, the higher temperature data contained a good deal of experimental





uncertainty. These limitations have obvious implications for the direction of future work on HCDA and core-melt chemistry.

5. PLANNED FUTURE WORK

Future experiments include dynamic laser system studies of the UO_2/PuO_2 -SS-Na (gas) system using x-ray, TEM, and electron diffraction analyses. Determination of the effects of fission-product additions on the hemical interactions of sodium and mixed-oxide fuel is a short-term goal. Characterization of species evolved from a boiling sodium pool is a long-term goal.

6. RECOMMENDATIONS FOR FUTURE WORK

The key to understanding the chemistry of HCDA and core-melt aerosols is the proposal of physical and chemical models for comparison of calculated observables to experimental results. In order to calculate the observable quantities associated with any model one must have the appropriate thermodynamic and kinetic data available. The unavailability of these data has been a very limiting constraint in HCDA and core-melt aerosol chemistry. We have been able, to a limited extent, to assess the applicability of an equilibrium thermodynamic model to sodium uranate formation. The disagreement with experiment shows that sodium uranate formation is not a thermodynamically controlled process. The thermodynamic results were of use, however, in rationalizing the experimental results in terms of a cooling curve/seed-out mechanism. Chemical kinetic data on sodium uranates and plutonates at realistic HCDA temperatures would be very helpful in understanding HCDA aerosol chemistry. In order to give a concise guide to what thermochemical and kinetic data have been determined and to what areas emphasis should be directed, the following outlin : has been constructed.

SUMMARY OF THERMOCHEMICAL AND KINETIC DATA ON THE Na-U-O and

Na-Pu-O SYSTEMS

Core-Melt Temperature Range (~700-900°C)

- I. Thermochemical Data
 - A. Systems studied = Na-U-O
 - 1. Type of data heats of formation for sodium uranates
 - Method high temperature Knudsen effusion/mass spectrometry
 - Reference J. E. Battles, W. A. Shinn, and P. E. Blackburn, J. Chem. Thermo., 4, 425 (1972).

- B. Systems, in need of study: Na-Pu-O
 - Type of data needed heats of formation and heat capacities
 - Probable best method high temperature mass spectrometry
 - 3. Feasibility feasible by same method as above (I-A-3).
- II. Chemical Kinetic Data
 - A. Systems studied mixed oxide (Pu/U+Pu=0.20) and sodium
 - Type of data rates determined from volume change versus time data
 - 2. Method metallographic microscopy
 - Reference Q. E. Martin and J. Schilb, in <u>ANL Fuels</u> and <u>Materials Chemistry Semiannual Report</u>, <u>Argonne</u> National Laboratory, Chemical Eng. Div. (July -December 1972), pp. 4-9.
 - B. Systems in need of study PuO₂/Na, UO₂/Na, more accurate data needed on mixed oxide/Na system
 - 1. Type of data rate constants for uranate and plutonate formation as functions of temperature
 - 2. Probable best method metallographic microscopy
 - Feasibility very feasible; same methods as used by Martin and Schilb will work with single oxides; accuracy of method can be improved by more careful experimental design.

HCDA Temperature Range (~900 to 2800°C)

- I. Thermochemical Data
 - A. Systems studied Na-U-O (extrapolation of data to highest part of temperature range may be questionable)
 - 1. Type of data heats of formation
 - 2. Method mass spectrometry
 - Reverences J. E. Battles, W. A. Shinn and P. E. Blackburn, J. Chem. Thermodynamics, 4, 425 (1972).

- B. Systems in need of study Na-Pu-O at high end of temperature range
 - Type of data heats of formation, high temperature heat capacities
 - 2. Method mass spectrometry/calorimetry
 - 3. Feasibility experimentally feasible
- II. Chemical Kinetic Data
 - A. Systems studied none
 - B. Systems in need of study Na-U-O, Na-Pu-O
 - Type of data rate constants and/or cross sections for uranate formation reactions and formation of intermediate gaseous species.
 - Method high temperature mass spectrometry, atom beam experiments, surface analysis
 - 3. Feasibility feasible, but requires large initial outlay for instrumentation and a high level research effort to achieve enough results to make reliable predictions.

In light of recent de-emphasis of the HCDA scenario and the high cost in both time and money to get kinetic data in the HCDA temperature range, these experiments are not recommended. Future efforts would be best directed toward collection of thermochemical data on the Na-Pu-O system by mass spectrometric methods similar to those used by Battles et al. on Na-U-O and toward rate data on U, Pu, mixed oxide systems by microscopic volume change measurements, essentially an extension of the work of Martin and Schilb. Both these efforts would generate data applicable to the core-melt temperature range. Since the methods are well established (not state-of-the-art) and the volume of data required is not too large, the cost effectiveness of these endeavors would be markedly greater than for the atom beam experiments of HCDA-II-B.

7. ACKNOWLEDGEMENTS

The authors would like to thank E. Stacy who operated the transmission and scanning electron microscopes and who photographed the aerosol particles and electron diffraction patterns which were used in this study. We would also like to thank D. R. Kaser for helping to design and set up the radioactive laser facility.

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- 2. W. A. Zanotelli, G. D. Miller, and E. W. Johnson, <u>1978 Annual</u> <u>Report: Aerosol Characterization from a Simulated HCDA</u>, <u>NUREG/CR-0740</u>, <u>MLM-2597</u> (1979).*
- 3. W. A. Zanotelli and G. D. Miller, <u>The Possible Mechanisms for</u> the Formation of the Observed and <u>Expected Compounds During a</u> <u>Hypothetical Core Disruption Accident (HCDA)</u>, <u>NUREG/CR-1134</u>, <u>MLM-2637 (1979).*</u>

*Available for purchase from the NRC/GPO Sales Program, U.S. Nuclear Regulatory Commission, Washington, D.C. 20555, and/or the National Technical Information Service, Springfield, VA 22161

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