NRC FORM 189
(3-81)

U.S. NUCLEAR REGULATORY COMMISSION

PROJECT AND BUDGET PROPOSAL FOR NRC WORK

DATE OF PROPOSAL: 8/1/83

☐ NEW
☒ REVISION NO.

PROJECT TITLE: High Temperature Fission Product Chemistry

FIN NUMBER: A-1227

NRC OFFICE: Office of Nuclear Regulatory Research

NRC B&R NUMBER: 60190201

DOE CONTRACTOR: Sandia National Laboratories

CONTRACTOR ACCOUNT NUMBER: DE-AC04-76DP00789

SITE: Albuquerque, NM 87185

DOE B&R NUMBER: 401001060

COGNIZANT PERSONNEL	ORGANIZATION	FTS PHONE NUMBER
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OTHER NRC TECHNICAL STAFF: Lisa Chan	NRC/RES	427-4715
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PERIOD OF PERFORMANCE
STARTING DATE: 10/1/83
COMPLETION DATE: 9/30/84

[redacted]

STAFF YEARS OF EFFORT (Round to nearest tenth of a year)	FY 83	FY 84	FY 85	FY 86	FY 87
Direct Scientific/Technical	4.3	2.9	3.5		
Other Direct (Graded)					
TOTAL DIRECT STAFF YEARS	4.3	2.9	3.5		
COST PROPOSAL					
Direct Salaries	444	300	412		
Material and Services (Excluding ADP)	143	34	54		
ADP Support	25	22	19		
Subcontracts		9	16		
Travel Expenses — Foreign	–	10	2		
Travel Expenses — Domestic	5	5	6		
Indirect Labor Costs					
Other (Specify)					
General and Administrative (%)					
TOTAL OPERATING COST	617	380	509		
CAPITAL EQUIPMENT FIN CHARGED: ______					
TOTAL PROJECT COST	617	380	509		

FY 84 MONTHLY FORECAST EXPENSE

OCTOBER	NOVEMBER	DECEMBER	JANUARY	FEBRUARY	MARCH
32	32	31	32	31	32
APRIL	**MAY**	**JUNE**	**JULY**	**AUGUST**	**SEPTEMBER**
32	31	31	32	32	31

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PROJECT TITLE

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DOE PROPOSING ORGANIZATION

Sandia National Laboratories

FORECAST MILESTONE CHART: Scheduled to Start – △——▲ – Completed (Shown in Quarter Year)
PROVIDE ESTIMATED DOLLAR COST FOR EACH TASK FOR EACH FISCAL YEAR

TASK		FY 83 (1st 2nd 3rd 4th)	FY 84 (1st 2nd 3rd 4th)	FY 85 (1st 2nd 3rd 4th)	FY (1st 2nd 3rd 4th)	FY (1st 2nd 3rd 4th)
Topical Report Reactions of B_4C	SCHEDULE	△———	——▲			
	COST	200	50			
Prepare Definitions of Data Needs	SCHEDULE	△—	—▲			
	COST	117	50			
Reactions of Te with Ag, Sn and Structural Materials	SCHEDULE	△———	———▲			
	COST	300	150			
Reactions of Cd with fission products	SCHEDULE		△——▲			
	COST		80			
Experimental investigations of Ru and Mo steam	SCHEDULE		△——	——▲		
	COST		50	509		
TOTAL ESTIMATED PROJECT COST		617	380	509		

PROJECT DESCRIPTION: (Provide narrative descriptions of the following topics in the order listed. Attach on plain paper to the NRC Form 189. If an item is not applicable, so state.)

1. OBJECTIVE OF PROPOSED WORK
2. SUMMARY OF PRIOR EFFORTS
3. WORK TO BE PERFORMED AND EXPECTED RESULTS
4. DESCRIPTION OF ANY FOLLOW-ON EFFORTS
5. RELATIONSHIP TO OTHER PROJECTS
6. REPORTING SCHEDULE
7. SUBCONTRACTOR INFORMATION
8. LIST NEW CAPITAL EQUIPMENT REQUIRED
9. DESCRIBE SPECIAL FACILITIES REQUIRED
10. CONFLICT OF INTEREST INFORMATION

SEE NRC MANUAL CHAPTER 1102 FOR ADDITIONAL INFORMATION

APPROVAL AUTHORITY—SIGNATURE: Dana A. Powers [signatures] 8/23 | DATE

6422 / 6420 0155 6400 6000

(1) Objective

The High Temperature Fission Product Chemistry program provides quantitative data and models on the behavior of fission products during severe reactor accidents. The primary thrusts of this research are to define chemical processes that affect fission product transport in the reactor primary system and to provide models of fission product behavior during severe accident processes. Quantitative data on the rates of fission product reactions with structural and aerosol materials in steam and hydrogen atmospheres are produced in this program. These data are used in computer models of severe reactor accidents such as TRAP-MELT. Mechanistic models of fission product release during fuel degradation, steam explosions, and core debris/concrete interactions are being developed in this program. The efforts in this program directly support the NRC's Interim Source Term Study.

2a) Summary of Accomplishments in FY83

Accomplishments in the High Temperature Fission Product Chemistry Program during FY83 may be categorized as those dealing with fission product transport in reactor primary systems and those dealing with fission product release during severe reactor accident processes. Studies of chemical interactions that will affect transport of fission products yielded the following results:

- The rate of CsOH and CsI reaction with Inconel 600 and type 304 stainless steel at 1000°C was found to be slow. Reaction of cesium iodide involves dissociation to release iodine or HI.

- The reactions of CsOH and CsI are with the trace constituents of the steel or Inconel.

- Rates of tellurium reactions with silver, tin, Zircaloy-2, oxidized stainless steel and oxidized Inconel in argon and in steam atmosphere at 500-800°C were measured.

- Desorption rates of tellurium bound to Inconel and stainless steel were measured and found to obey Arrhenius kinetics.

- Boron carbide control rod material was found to react with steam and the products of this reaction react with CsOH and CsI. HI or I may be a product of the reaction with CsI.

These results point to two substantive findings in FY83. First, there is a competition between reaction of fission products with structural materials so they cannot escape the primary system and

reaction of fission products with aerosols that can be carried from the primary system. Second, non-fuel materials such as boron carbide can affect the fission product chemical form and transport behavior.

During FY83 the VANESA model of fission product release during core debris/concrete interactions was formulated. This model was used to calculate releases expected during severe accidents at the Surry, Peach Bottom, Grand Gulf, Zion and Sequoyah plants as part of the Interim Source Term Study. Further support for the Interim Source Term Study was provided in the conceptual formulation of models for fission product release during steam explosions and during fuel melting.

2b. Discussion of Accomplishments in FY83

The reactions between cesium-iodine compounds with structural materials in steam and hydrogen atmospheres were under study in FY83. Two stable fission product species predicted to exist in these environments are CsOH and CsI. At 1000°C the reaction of CsOH with Inconel and of CsI with Inconel and with 304 ss were all slow but the reaction rates were measured and could be calculated with the CRCDEP code. (CRCDEP is a calculational model that has been developed in this program for predicting reaction rates of vapor depositing on the walls of a pipe with circular cross section.) No iodine was found in the products of CsI reactions with surface layers on either the Inconel or type 304 stainless steel.

At the lower temperatures of 700C and 850C, CsOH reacted to form particles on the 304 ss surface. The particles have been found to consist of cesium and chlorine at 700C and cesium, phosphorus, manganese and nickel at 850C. If these particles formed in the steam stream, they nucleated and grew to their 10 to 50 µm size in several seconds.

These results are being interpreted in terms of a tendency for CsOH to react with volatile species of minor elements in the steel. The products of reaction condense under the test conditions which simulate conditions in the primary system of a reactor during a severe accident.

Reaction rates were measured for tellurium on a variety of reactor materials (304 ss and Inconel 600 as-received and preoxidized) in argon in the temperature range of 500C to 800C. Measurements have been made under similar conditions for tellurium reacting with silver, Zircaloy-2 and UO_2. Tellurium reacted very rapidly with silver producing silver telluride whiskers which grew to several millimeters in length. The slight reaction of tellurium with Zircaloy at 500C, increased at 800C

until about 10% of the tellurium reacted with the zircaloy in the microbalance geometry. The rate of tellurium reaction with Zircaloy is controlled apparently by a surface oxide which forms easily and inhibits reaction at lower temperatures but tends to dissolve at higher temperatures. Tellurium reacts very slowly with UO_2 at 500C. About 7×10^{-6} gm/cm^2 are absorbed in a bed of 0.1 mm UO_2 particles over a several hour period; the tellurium desorbs from the UO_2 at 800C.

The reaction of tellurium with preoxidized Inconel 600 was found to be somewhat slower than with Inconel in the as-received condition. Nickel telluride reaction compounds changed from the leading edge to the trailing edge of the Inconel coupon and were identified. The rate of diffusion of metals through the reaction layer and the thickness of the layer control the reaction rate and the composition of the product. Several percent of hydrogen appears to have no effect on the reaction between tellurium and Inconel.

The desorption of tellurium from metals was studied. At temperatures greater than 800C, tellurium desorbed from Inconel which had been previously exposed to tellurium. Specific desorption rates were measured as a function of temperature using samples of $Ni_{2.86}Te_2$ (which had formed on Inconel) and $Fe_{2.25}Te_2$ (which had formed on 304 ss). With the iron telluride, additions of hydrogen to the argon-tellurium stream had no effect on the desorption. However, hydrogen decreased the stability of the nickel telluride by a factor of about five.

A series of experiments were begun in the steam facility to examine reaction rates of tellurium with structural materials in steam and hydrogen. Absorption of tellurium on Inconel indicates the reaction rate is rapid and similar to the results for tellurium reacting in argon. The same is true of tellurium reacting with 304 ss although the almost 100X thicker oxide layer made it more difficult to detect an equal amount of absorbed tellurium. The model CRCDEP is being used to estimate rates for the tellurium-in-steam reactions.

In the tellurium desorption experiments performed in a transpiration apparatus, an alumina boat containing tin was placed downstream of the tellurides. The molten tin extracted from the stream 60% to 75% of the tellurium at 700C and 75% to 90% at 900C. This semiquantitative experiment indicates that tin vaporized from Zircaloy fuel cladding could be an efficient scavenger for tellurium and might bind the tellurium so it could not react with structural materials.

Studies began on the control rod material boron carbide (B_4C) in a steam and hydrogen environment. At 1000C boron carbide oxidized in steam to form volatile boric acids. The boric oxide vapors condensed in cooler regions of the system plugging the 2.5 cm diameter condenser tube. The plug, porous to non-condensing gases, could act as a particle filter and react with the gases and particles. The boric acids could behave in a similar way in the cooler, small channel regions above a reactor core.

When CsI was added to the steam downstream of the B_4C a significant amount of cesium was found in the B_2O_3 product of B_4C oxidation. This indicates a probable reaction between CsI and boric oxide. Smaller amounts of cesium were found on the Inconel so either CsI or a cesium-boron compound has reacted with the Inconel. No iodine was found on either the B_2O_3 or the Inconel but some was found in the condensed acid plug. A reaction that could produce a more stable cesium-boron compound might release iodine in the form of HI.

When CsOH, instead of CsI, was injected into the steam, reactions between cesium and B_4C and between cesium and Inconel were similar to those observed with CsI.

Calculations suggest Cs_2MoO_4 is a stable cesium species within the fuel rod. Several experiments suggest it may not be stable in the primary system of a reactor during a severe accident. In a flow of argon Cs_2MoO_4 did not evaporate at temperatures up to 1000°C. Addition of H_2 to the argon led to evaporation beginning at temperatures of about 600°C. Mass loss accelerated above the melting point of Cs_2MoO_4. Addition of water vapor to the H_2 stream decreased the mass loss. CsOH appears to be the vaporizing species.

Raman spectra of tellurium, steam, and HI were calibrated with the laser-Raman spectrometer against the spectrum of nitrogen. A flowing system was developed to calibrate spectra of those fission product species that are corrosive to quartz, used for closed cell calibration. The flowing system can handle any carrier gas including steam. CsI and CsOH are being calibrated in an argon carrier and then their behavior in steam and hydrogen will be examined.

The VANESA model of aerosol and fission product release during core melt/concrete interactions has been formulated. Generation mechanisms included in the model are:

1. Vaporization of the species at high temperatures encountered in the melts which is accentuated by sparging gases from decomposing concrete.

2. Aerosol formation by bubble bursting.

These processes have been compiled in the model to determine:

1. The release rate of refractory species
2. Composition and properties of the released material
3. Size distribution of the aerosols formed in the release process

Predictions of the VANESA model compare well to predictions from an empirical correlation of experimental data on aerosol mass generation. The model predicts that at later times in an accident, release will be dominated by aerosol created when bubbles burst at the melt surface. This would provide a small but long term source of fission products to the containment atmosphere. Model sensitivity of vaporation release was found to be linear for gas flow through the melt and for activity coefficients of the melt constituents. Sensitivity of release to melt temperature is exponential.

Steam explosions were identified in the Reactor Safety Study as a mechanism of fission product release during severe reactor accidents. Ruthenium release during steam explosions was estimated to be important. Analyses done as part of the High Temperature Fission Product Chemistry program suggest that either chemical conditions will not favor ruthenium release during steam explosions or the time available for release will not be long enough to achieve significant release fractions. A conceptual framework for a model of fission product release during steam explosions has been formulated. This model utilizes data from steam explosions research to describe the nature of debris hurled into the atmosphere and yielding fission products. The detailed chemical kinetics of release and the duration of the release process are calculated.

Results obtained with this model are being used in the Interim Source Term Study.

3a. <u>Anticipated Accomplishment in FY84</u>

The activities in this program during FY84 will concentrate on the acquisition of experimental data needed for the analysis of fission product behavior during severe accidents. Limitations of resources will require curtailing model development activities. Careful definition of the chemical systems to be examined experimentally will be an important feature of work during FY84. The anticipated activities in FY84 are:

- Document results obtained in FY83 on the tellurium desorption rates in steam.
- Document results obtained in FY83 on the behavior of B_4C in steam with cesium hydroxide and cesium iodide.
- Conduct experiments to determine the effects of cadmium on the behavior of CsI, CsOH, and Te in steam.
- Conduct experiments to determine the nature of competitive reactions of Te with structural materials and with potential aerosol materials such as tin from zircaloy cladding.
- Conduct experiments on the behavior of Mo and Ru in steam and hydrogen.
- Model the effects of clad interactions with fuel on the release of fission products.

Milestones

1st Quarter FY84

(1) Complete topical report on boron carbide reactions with steam, CsOH and CsI.

(2) Complete topical report on tellurium reactions and desorption in steam.

(3) Prepare definitions and background material for the next experimental studies.

2nd Quarter FY84

(4) Conduct experiments to evaluate competitive reactions of Te with tin, silver, and structural materials.

3rd Quarter FY84

(5) Topical report on the competitive reactions of Te.

(6) Initiate experiments to explore the behavior of cadmium.

4th Quarter FY84

(7) Topical report on cadmium behavior in steam and reactions with Te, CsI, and CsOH.

(8) Topical report on the thermodynamics of the $Zr-ZrO_2-UO_2$ system.

(9) Initiate experiments on the behavior of Mo and Ru in steam.

3b. Discussion of Activities in FY84

Experimental data on the chemistry of fission products needed for NRC activities may be categorized as (1) data needed for severe accident analysis models, and (2) data needed to interpret results of experiments. Data needed by the TRAP-MELT model of fission product transport in the primary system are good representatives of the first category. Data needed to interpret fission product release results from the PBF tests of fuel degradation, and data for interpreting and analyzing results of the Marviken fission product transport tests represent the second category. It is the objective of the High Temperature Fission Product Chemistry program to supply chemistry data in both categories.

A large number of experimental results were obtained in FY83. Documentation of these results will occupy a substantial portion of the first quarter of FY84. Results obtained in experiments with tellurium reaction in steam with metals and the behavior of B_4C in steam with CsOH or CsI will be completed in the first quarter. Also during the first quarter of FY84 plans will be formulated for further investigations of fission product chemistry in the steam and hydrogen environment of the primary system during a severe reactor accident. These plans will, at the end of the first quarter, be reviewed with the NRC.

At this juncture the most pressing data needs involve the following systems:

(1) Competitive reaction of tellurium with structural and aerosol materials.

Previous work in this program has shown tellurium firmly and rapidly binds to structural materials found in reactor cores such as stainless steel. Once bound the tellurium would not be able to contribute to the fission product release to the containment or from the reactor plant. On the other hand, it has been shown that tellurium reacts efficiently with aerosols such as silver from control rods or tin expelled during fuel clad oxidation. Tellurium bound to these aerosols will contribute to the fission product source term to the extent the aerosols contribute. A competition then exists in the reactions of tellurium which must be evaluated to determine the Te source term. This competition may explain why tellurium was able to pass

so far down the experiment train during the recent fuel degradation test at PBF.

(2) Effects of cadmium on the behavior of CsOH, CsI, and Te.

Experiments to determine fission product release done at ORNL and at KfK in Germany have shown that cadmium is vaporized easily. Large quantities of cadmium vapor could be expected during severe accidents at nuclear plants that use precious metal (Ag-In-Cd) control rod alloys. Cadmium is a reactive element and forms stable halides and tellurides. The presence of cadmium vapors could, then, alter the behavior of CsI and Te especially the reactions of these fission product species with structural materials. Reaction of cadmium vapors with structural materials could prevent formation of copious cadmium aerosols in cooler regions and avoid the effects these aerosols could have on agglomeration or settling of fission product aerosols.

(3) The behavior of Mo and Ru in steam containing CsI, CsOH, and Te.

Volatile molybdenum oxides can be formed in steam environments. These oxides ought to be reactive toward Te and may, in fact, react with CsI. Ruthenium ought not be volatile in these environments, yet some ruthenium release and transport was observed in the recent PBF test. Some have argued that gaseous RuTe was responsible for this release.

(4) The behavior of alkali metal fission products in steam.

The volatility of barium and strontium during severe reactor accidents may be higher than estimated in the Reactor Safety Study in which stable, gaseous hydroxides were neglected. On the other hand, the alkali metals can react with ZrO_2 to form stable, low volatility zirconates. The rate at which alkali metal vapors react with ZrO_2 is not known so the potential mitigation of alkali metal release cannot be evaluated.

(5) Effect of manganese aerosols on Cs, I, and Te transport.

Manganese from steel is expected to be a major, non-radioactive, contributor to the aerosol produced during a severe reactor accident.. The Marviken experiments will use manganese as a major constituent of its "corium" aerosol simulant. Data from the Marviken experiments are to be used to validate predictions of aerosol and fission product transport by the TRAP-MELT code. It will be essential then

to provide deposition velocity data to the TRAP-MELT code on the behavior of manganese species and their interactions with "fissium" constituents such as Te, CsI, and CsOH.

At the current level of effort it is feasible to investigate during FY84 the first three of these tasks. Prior to initiating experimental work detailed plans for the experiments and description of the thermochemical and kinetic basis for the experiments will be prepared for NRC and peer review.

Model development in this program will be curtailed during FY84 relative to FY83. A single objective of establishing a thermochemical description -- suitable for computer codes -- of the effects of clad/fuel interactions on fission product release is foreseen. This model will be based on the experimental data being generated by researchers in West Germany. It will attempt to describe in mathematical form the changes in fission product activities brought on by dissolution of cladding in the fuel to form a low melting material.

4. Anticipated Activities in FY85

Experimental investigation begun in FY84 will be completed. Studies of the behavior of alkali metal fission products and the behavior and interactions of manganese aerosols with fission products will begin.

5. Related Activities

Results from the High Temperature Fission Product Chemistry program are of direct use to current reactor licensing activities concerning the extent and chemical forms of fission product release during severe accidents. In addition, results of this work are of direct use to other NRC-sponsored research activities. Experimental reaction and thermodynamic data are used in the TRAP and TRAP-MELT codes being developed at Battelle Columbus Lab. The diagnostic methods using Raman spectroscopy could be used by ORNL for the study of fission product release from fuel rods. A close cooperation with these users of the research results is being maintained.

Allied work on fission product release from high temperature core materials is underway in Germany. Regular, formal, information exchanges and frequent informal visits among the staff insure that results of the German work are considered in this activity and that there is no unnecessary duplication of effort.

6. Publications

1. R. A. Sallach, C. J. Greenholt, and A. R. Taig, Chemical Interactions of Tellurium Vapors with Reactor Materials, NUREG/CR-2921, SAND82-1145, Sandia National Laboratories, July 1983.

2. R. A. Sallach, R. M. Elrick, and A. R. Taig, Reaction Between Some Cesium-Iodine Compounds and Reactor Materials: 304ss, Inconel 600 and Silver, NUREG/CR-3197, SAND83-0395, Sandia National Laboratories, September 1983.

3. D. A. Powers and J. E. Brockmann, "Release of Fission Products and Generation of Aerosols Outside the Primary System", Appendix C in Radionuclide Release Under Specific LWR Accident Condition, Vol. 1 (draft BMI-2104).

4. D. A. Powers and J. E. Brockmann, "Status of VANESA Validation", contribution to Vol. 5, BMI-2104.

5. D. A. Powers, "A Model of the Steam Explosion Source Term, Sandia Topical Report.

Anticipated Reports in FY84

1. D. A. Powers, "Vaporization of Cadmium from Reactor Control Rods", Sandia Topical Report.

2. R. Elrick, et al., "Tellurium Reactions and Desorption from Steels in Steam", Sandia Topical Report.

3. R. Elrick, et al., "Reactions of B_4C in Steam with CsOH and CsI", Sandia Topical Report.

4. R. Elrick, et al., "Reaction of Tellurium with Tin and Silver in Steam", Sandia Topical Report.

5. R. Elrick, et al., "Reactions of Cadmium with Steel, CsI, and Te in Steam", Sandia Topical Report.

7. Subcontractor Information

NA

8. Equipment Purchases

No major equipment purchases are anticipated.