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UC-80 — Reactor Technology

POTENTIAL METAL-WATER REACTIONS IN LIGHT-WATER-COOLED POWER REACTORS

Howard A. McLain

NUCLEAR SAFETY INFORMATION CENTER

NSIC

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Nuclear Safety Information Center

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Howard A. McLain

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AUGUST 1968

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FOREWORD

The recent surge in the building of large nuclear power plants, particularly with the projected desirability of using urban sites for such installations, has focused attention on many aspects of the AEC's responsibilities for licensing reactors and insuring the public safety. Since the industry is "young," meaningful, long-term operating experience is sparse and the definition of the possible accident spectrum, as well as a set of firm design requirements, is subject to a largely analytical approach that necessarily involves conservative judgments. As plant designs become standardized and operating experience on the newer large reactors is gained, the inevitable process of refinement and of acquiring confidence in the operation of the plants will occur. This relatively slow evolutionary approach to acquiring firm design standards and criteria is not felt to be conducive to achieving the great national benefits of atomic energy within a reasonable time, in terms of the conservation of resources, combating air pollution, and the multitude of gains resulting from low-cost electricity.

As part of the effort to improve on this approach, the Regulatory Review (Mitchell) Panel recommended the formation by the AEC of a Steering Committee on Reactor Safety Research to coordinate the needs of the Regulatory Program with the direction of the safety research and development programs. This committee, in turn, recommended that several studies be undertaken to provide guidance for the research and development projects, and this was, in turn, implemented by the AEC Division of Reactor Development and Technology into the series of discussion papers herein described. It was intended that these papers provide a comprehensive assessment of the present status of specific aspects of nuclear safety and, by identifying accepted technology and the technology needing further experimental verification, that they enhance the understanding and confidence in this new industry.

Accordingly a number of the safety aspects of large light-water power reactors were selected by the AEC* as subjects for detailed study to

*Letter from Milton Shaw (Director, AEC Division of Reactor Development and Technology) to ORNL, March 28, 1966.

ascertain whether gaps in knowledge exist and where a research and development program could be of benefit. The subjects selected cover many of the areas for which inadequate factual bases exist and in which research that duplicates expected conditions is very difficult to perform. In general the subjects are in areas considered critical in the safety analysis of power reactor installations. Eight subjects were identified and a state-of-technology type of discussion paper was prepared on each. The papers, which are directed primarily toward a technical-management audience, generally compare existing or planned plant applications with what is capable of being done at this time. Such comparisons have helped to identify inadequacies in assumptions, available data, or general basic knowledge so that, together with the opinions of experts in a particular field, areas of meaningful research and development have been identified.

This paper is one of the series of eight companion papers listed below:

<u>Title</u>	<u>Author</u>	<u>ORNL-NSIC No.</u>
Missile Generation and Protection in Light-Water-Cooled Power Reactor Plants	R. C. Gwaltney	22
Potential Metal-Water Reactions in Light-Water-Cooled Power Reactors	H. A. McLain	23
Emergency Core-Cooling Systems for Light-Water-Cooled Power Reactors	C. G. Lawson	24
Air Cleaning as an Engineered Safety Feature in Light-Water-Cooled Power Reactors	G. W. Keilholtz, C. E. Guthrie, and G. C. Battle, Jr.	25
Testing of Containment Systems Used with Light-Water-Cooled Power Reactors	F. C. Zapp	26
Review of Methods of Mitigating Spread of Radioactivity from a Failed Containment System	R. C. Robertson	27
Earthquakes and Nuclear Power Plant Design	T. F. Lomenick and C. G. Bell	28
Protection Instrumentation Systems in Light-Water-Cooled Power Reactor Plants	C. S. Walker	29

Although not specifically one of this series, a related discussion paper on reactor pressure vessels, ORNL-NSIC-21, edited by G. D. Whitman, G. C. Robinson, and A. W. Savolainen, has also been prepared at ORNL.

The general approach in the preparation of these papers was to select a primary author-investigator knowledgeable in the subject area and to establish committees of experts to review the work at several stages during its preparation. Review groups were formed both from within ORNL and outside. The external review committee members were drawn principally from other national laboratories, universities, and private research institutes - in all, 52 individuals participated and are identified in the reports. In some cases, part of the material used was developed and/or written by a subcontractor, who is similarly identified. In all cases, correspondence and/or visits were made to many sources of information, particularly to reactor operators, suppliers, architect-engineers, and public utilities, as well as to the appropriate national laboratories. This wide use of acknowledged experts was made in an attempt to include their opinions and knowledge toward the ultimate goal of achieving, through intensive research and development programs, well-defined design criteria to insure the public health and safety and to maintain a viable nuclear power industry. However, in all instances the authors have expressed conclusions and recommendations that reflect their own judgment and not that of any particular group, such as the AEC, reactor designers, or utilities.

In most subject areas more information was developed than it has been possible to include in the body of the reports prepared in this series. In some instances, such information has been included in the appendices and in other instances this information will be included in more technically oriented reports to be published in the near future. In addition, it is expected that additional discussion papers will be written on some of the many other safety aspects of large water-cooled reactors, as well as other types of reactors as they come into wider usage.

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ACKNOWLEDGMENT

The role of metal-water and associated chemical reactions in the unlikely event of a reactor accident was discussed with more than 50 people interested and knowledgeable in this field. These individuals include those serving on the review committees for this report, listed in Appendix A, and those visited regarding this subject, listed in Appendix B. In addition, much help and suggestions were obtained from S. E. Beall, W. B. Cottrell, and J. W. Michel of ORNL.

It is difficult to single out individuals who contributed more than others to this study, and no attempt is made to do so. All showed interest and gave freely of their information and suggestions. Without their interest and help, the preparation of this paper would have been more difficult or even impossible.

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ABSTRACT

The available data regarding the role of chemical reactions in the unlikely event of a light-water power reactor accident were collated and reviewed. These reactions must be considered as only one of the many aspects of a reactor accident, and only by considering an integral model of the accident can they be assessed realistically. Compared with the situation regarding the definition and mathematical simulation of the reactor accident, the basic kinetics of the chemical reactions are well understood.

Contributions of the metal-water reaction to the consequences of a nuclear-excursion accident appear to be minor compared with the other aspects of these accidents. In a loss-of-coolant accident, prompt initiation of emergency core-cooling systems would limit the amount of metal-water reaction to a low value. However, possible fragmentation of fuel pins having chemically reacted cladding makes it difficult to interpret quantitatively the criterion that the cladding metal-water reaction is to be limited to negligible amounts. Without the use of emergency core-cooling systems, it appears that the amount of metal reacted prior to the melting of the reactor core would be between 25 and 50%. Hydrogen explosions are not usually considered credible, since hydrogen produced by the metal-water reaction is assumed to be below its flammability limit or is assumed to burn upon entry into the containment vessel. Although there is much information to back up these assumptions, more work should be done regarding the detonation limits of hydrogen-air-steam mixtures and the possible pocketing of hydrogen within containment vessels.

1. INTRODUCTION AND SUMMARY

1.1 Purpose and Scope of this Review

The mechanisms of accidents and the means of coping with them, regardless of how unlikely their occurrence may be, must be considered in the design of a nuclear reactor. This is necessary in order to be able to assure the public that the reactor is not a hazard because of its inventory of radioactive materials. For the radioactive materials to reach the reactor environs, the fuel-rod cladding, the primary coolant system, and the containment vessel must all fail. Energy is required to cause failure of these components and systems, and sources of this energy could be fission energy, stored or sensible energy, heat released by decaying fission products, or heat released by chemical reactions. The chemical reactions and the part they play in nuclear reactor accidents are discussed in this review. As will be seen later, the role of these reactions in accident situations must be understood in order to assess their effects correctly. However, chemical reactions are only one segment of an accident, and considering them in other than integral models of accidents might yield misleading results.

The role of chemical reactions in a loss-of-coolant accident has been considered to some extent in the review of this hypothetical accident in large power reactors by a special task force headed by Ergen.¹ This role also has been considered by Lawson² in his review of emergency core-cooling systems, which is a companion report to this one. The draft of the "Water-Reactor Safety Program Summary Description,"³ prepared by the Water-Reactor Safety Program Office, is also pertinent. It summarizes the various light-water reactor safety research and development projects sponsored by the USAEC, including work on chemical reactions, and describes how these projects are related to the hypothetical reactor accidents and to each other.

Most of the reactors built or being built for commercial power generation in this country are of the pressurized-water or boiling-water types, and these are the only types considered in this review.

This review is further limited to those reactors for which preliminary design and safety analysis reports are available. These reactors contain substantial quantities of stainless steel and/or zirconium that could possibly react with water or steam in an abnormal situation. In addition, hydrogen is produced from these reactions, and it could react with the air in the reactor containment vessel.

Projected power outputs from the commercial reactors ordered recently are generally higher than those from the existing reactors and those ordered previously.^{4,5} Reactors of higher power output contain larger quantities of metal, have higher inventories of radioactive materials, and often have higher power densities. This trend toward larger reactors contributes to the growing problem of site selection for these reactors. Traditional practice for siting reactor plants requires an exclusion area, a low-density population zone, and a specified population-center distance.⁶ These zones and distances become larger as the power is increased, and the number of economical sites that meet the requirements becomes limited.⁷ For a site to be economical, the electrical transmission costs must be kept to a minimum and there must be a sufficient cooling water supply for the turbine condensers. In order to use sites that do not meet the traditional requirements, it will be necessary to have a better understanding of the consequences of unlikely reactor accidents and, if required, to develop more reliable methods to cope with them.

The present approach used by reactor manufacturers to make the best use of existing sites and to assure themselves that the reactor does not become a hazard is to design the reactor plant with several lines of defense.¹ The first line of defense is a design that will provide for safety in normal operation and will have a large tolerance for any abnormal operation or component failure. This requires that the reactor plant be built to high standards set by very competent designers. Once the basic reactor plant has been designed, the second line of defense is to give attention to the design of the components which, if they malfunctioned, could cause serious accident consequences. These components are designed on a much more conservative than normal basis to incorporate

fail-safe features and redundancy, where applicable, and exceptional quality control is specified in their fabrication. As a third line of defense, engineered safety features are incorporated into the reactor plant to prevent it from becoming a hazard if one or more of these critical components does fail. These safety features are designed to the same high standards as the reactor components to insure that they will operate when needed. The reactor plant is then analyzed in terms of the hypothetical accident in which these safety features fail. This analysis may result in the incorporation of additional safety devices in the reactor plant.

In spite of all the design conservatism and the use of engineered safety features, an accident can always be hypothesized in which some component or system in the reactor plant, along with the appropriate protective devices, will fail. As will be seen, it is currently impossible to design a practical reactor plant that is infallibly safe in terms of the surrounding public. The reactor can only be designed so that the probability of it becoming a hazard to the public is extremely remote.

It is not the intent of this report to review the reliability or the probability of failure of the reactor system, its components, or the engineered safety features. This review discusses the events in reactor accidents from the viewpoint of the chemical reactions that could possibly occur during such accidents. As will be seen, there is almost a definite threshold for the chemical reactions that can take place in a light-water reactor during an accident if they are considered relative to the effectiveness of the engineered safety features. If the safety devices operate as designed when required, little or no chemical reaction will take place during the reactor accident. If they failed to operate or failed to operate properly, the consequences from the accident, including the chemical reactions, could be serious. Because of this threshold, much of the discussion in this report is directed to the situation in which these safety features have failed to operate properly when needed.

This report is organized into two parts. The first part presents basic information regarding metal-water and associated chemical reactions and the results of experiments with fuel-pin samples under simulated reactor accident conditions. The second part describes the application of this information to the prediction of the rate and extent of these reactions in reactor accidents. Pertinent experimental work is discussed in each of these parts, and the assignment of any one of these tests to the respective parts is somewhat arbitrary.

For the application of metal-water and associated chemical-reaction data to hypothetical accidents of commercial power reactors, many assumptions and involved calculations are necessary because the rate and extent of these reactions are dependent on the thermal-hydraulic history of the accident. Mention is made of the methods and computer programs being used to calculate this information, along with discussions of some of their merits and possible shortcomings; however, a critical review of these methods and programs was beyond the scope of this study. As a result of this limitation, this report should not be regarded as an evaluation of a given reactor or of the merits of one reactor compared with those of another from the viewpoint of the chemical reactions. However, omission of the references in the second part of this report to the application of chemical-reaction data to hypothetical accident situations would, in my opinion, limit the usefulness of this review and cause many misleading interpretations.

1.2 Possible Metal-Water and Associated Reactions

1.2.1 Metal-Water Reactions

Chemical reactions between metals and water and/or steam usually are described by relations⁸ having the form

This reaction is thermodynamically possible for several metals, and a number of them, together with their reaction products, for which data were taken from Refs. 8 to 15, are listed in Table 1.1. It can be seen that the reaction of water or steam with zirconium or stainless steel

Table 1.1. Physical Properties of Materials and Energies Associated with the Metal-Water Reaction

Material	Density (g/cm ³)	Melting Point (°C)	Reactant Temperature (°C)	Reactant State	Oxide State	Oxides Formed	Oxide Melting Point (°C)	Heat of Reaction with Water ^a			Hydrogen Released from Metal-Water Reaction ^b		Heat of Reaction of Released Hydrogen ^b	
								cal/g	Btu/lb	Btu/in. ³ Metal	Liters (STP)/g Metal	ft ³ (STP)/in. ³ Metal	Btu/lb Metal	Btu/in. ³ Metal
Zirconium	6.5	1852	1852	Liquid	Solid	ZrO ₂	2700	1560	2805	659	0.491	1.847	2350	549
Stainless steel ^c	8.0	1370-1500	1327	Solid	Solid	Fe ₃ O ₄ ^d	1400-1550	254	457	133	0.51	2.361	2441	705
			1400	Liquid	Liquid	Fe ₃ O ₄ ^d		155	279	81				
Aluminum	2.7	660	660	Liquid	Solid	Al ₂ O ₃	2045	4200	7560	737	1.246	1.947	5963	579
UO ₂	10.8	2800	1200	Solid	Solid	UO ₂ .31	<2400	~0	~0	~0	0.017	0.106	84	33
			1500			UO ₂ .17	2500				0.014	0.088	68	26
			2727			UO ₂ .12	2670				0.010	0.063	48	19

^aHeats of reaction are based on 1 g or 1 lb of reactant.

^bIn the case of UO₂, these values are for 1 lb or 1 in.³ of oxide.

^cMelting temperatures and heats of reaction for stainless steel vary because they are dependent on the exact alloy composition, degree of the oxidation of iron, and the physical state of the oxides.

^dExperiments indicate that the overall stoichiometry of the stainless steel-steam reaction is the formation of Fe₃O₄ (Ref. 9). However, at any local spot, the degree of the oxidation of iron can vary from FeO to Fe₂O₃. In addition to Fe₃O₄, small amounts of FeCr₂O₄, NiFe₂O₄, and NiCr₂O₄ possibly could be formed.

could liberate substantial quantities of heat, which could augment the consequences of an unlikely reactor accident. However, reaction of steam with uranium dioxide at temperatures greater than 1200°C is limited, and little if any heat is liberated. It is possible that this particular reaction is slightly endothermic.¹⁵

1.2.2 The Hydrogen-Air Reaction

Hydrogen produced from metal-water reactions can react with the oxygen in air and liberate substantial quantities of heat according to the reaction

This reaction would probably occur in the form of burning hydrogen, but there is a possibility that it could be explosive or result in detonations. In that eventuality the resulting temperatures and forces could violate the integrity of the containment vessel.

1.2.3 The Metal-Air Reaction

Metal can react with the oxygen in air as well as with water and/or steam; a stoichiometric relation describing this reaction follows:

Several of the materials for which this reaction can occur are listed in Table 1.2, along with their reaction products and their heats of reaction.⁸ Because water-reactor accident situations usually are those in which steam or water atmospheres predominate, consideration of the reaction with air in accident analysis reports is limited. However, if the metals listed in Table 1.2 do come in contact with air at high temperatures, they will react.

1.2.4 Other Possible Chemical Reactions

Other chemical reactions can occur during a reactor accident in addition to those mentioned above. The UO_2 fuel can react with the zirconium cladding, and eutectics can be formed between UO_2 , uranium,

Table 1.2. Energies Associated with the Metal-Air (Oxygen) Reaction

Material	Reactant Temperature (°C)	Oxides Formed	Reactant State	Oxide State	Heat of Reaction with Oxygen ^a		
					cal/g	Btu/lb	Btu/in. ³ Metal
Zirconium	1852	ZrO ₂	Liquid	Solid	2,883	5,189	1,219
Stainless steel ^b	1370	FeO, Cr ₂ O ₃ , NiO	Liquid	Solid	1,330-1,430	2,394-2,574	692-744
Aluminum	660	Al ₂ O ₃	Liquid	Solid	7,487	13,477	1,315
Hydrogen	1000	H ₂ O	Gas	Gas	29,560	51,408	

^aHeats of reaction are based on 1 g or 1 lb of reactant.

^bMelting temperatures and heats of reaction for stainless steel vary because they are dependent on the exact alloy composition, degree of oxidation of iron, and the physical state of the oxides.

zirconium, and ZrO_2 .¹⁶⁻²¹ Eutectic formation between UO_2 and stainless steel oxides at temperatures near the melting point of stainless steel has also been observed.²²⁻²⁴ Because of these and other complicating factors, the melting and the slumping mechanisms of the fuel pins are not well understood. Also, in the case of fuel with zirconium cladding, the stainless steel structure in the core region can form low-melting eutectics with any zirconium that may have come in contact with it. The zirconium-iron phase diagram indicates that these eutectics could have melting points as low as 934°C (Ref. 25).

As will be seen later, hydrogen formed by the metal-water reaction in one part of the core could possibly be absorbed in another part of the core. Experimental data for the absorption of hydrogen in zirconium at the higher temperatures encountered in the accident situations are limited,²⁶⁻²⁸ but the zirconium-hydrogen phase diagram indicates that appreciable amounts of hydrogen could be dissolved in zirconium.²⁹⁻³³ Factors complicating this situation are that (1) higher pressures are required for the high-temperature absorption of hydrogen³³ and (2) small amounts of water (10 to 100 ppm) in the gas stream retard its absorption.¹⁹

1.2.5 Magnitudes of Potential-Energy Release from Chemical Reactions

The magnitudes of the energies associated with metal-water and hydrogen-air reactions can be rather significant. Examples of these energy sources for the Indian Point-2 (PWR)³⁴ and the Browns Ferry (BWR)³⁵ reactors are given in Table 1.3. It can be seen that if all the zirconium in these reactors reacted with water or steam and if all the hydrogen formed reacted with air, the chemical-energy release would have the same order of magnitude as the energies associated with the stored internal heat within the reactor and with the core decay heat. Fortunately there are many factors that limit the rate and the extent of these chemical reactions in these reactors. With engineered safety features in operation, less than 1% of the metal will react. It can be seen in Table 1.3 that the energies associated with 1% chemical

Table 1.3. Potential Energy that Could Be Released in an Accident of the Indian Point-2 (PWR) or the Browns Ferry (BWR) Reactors

	2758-Mw(th) Indian Point-2 Reactor		3293-Mw(th) Browns Ferry Reactor ^a	
	Btu	Mwhr	Btu	Mwhr
Primary coolant internal energy	3.00×10^8	87.9	3.30×10^8	96.7
Hot reactor coolant system metal	0.18×10^8	5.3		
Core-stored heat			0.20×10^8	5.9
Core decay heat integrated for first 1/2 hr of accident	1.50×10^8	44.0	1.55×10^8	45.4
100% Zr-H ₂ O reaction	1.13×10^8	33.1	3.80×10^8	111.3
100% H ₂ -O ₂ reaction	0.88×10^8	44.0	3.10×10^8	90.8
1% Zr-H ₂ O reaction	0.01×10^8	0.3	0.04×10^8	1.1
1% H ₂ -O ₂ reaction	0.01×10^8	0.4	0.03×10^8	0.9

^aThe zirconium-water and hydrogen-oxygen reaction values for the Browns Ferry reactor are based on Zircaloy both in the cladding and in the fuel-element shrouds.

reaction are small compared with the sources of potential-energy release within the reactor. Of course, the spatial-time history of the energy release within a reactor during a postulated accident is not shown in this table, and this is very important in assessing the consequences of such an accident. Therefore it can be seen that while the chemical reactions are not the predominate energy source in a reactor accident, they cannot be ignored.

1.3 Situations in Which the Metal-Water Reaction Could Occur

1.3.1 Requirements for the Metal-Water Reaction

The first requirement for a chemical reaction to take place is, of course, to bring the reactants together physically. Also, as will

be seen later, no noticeable chemical reaction will take place until the metal temperatures are substantially higher than those present in a normal operating reactor. This implies that the metal-water reaction is highly dependent on the heat transfer and fluid mechanics of a given reactor accident. These characteristics are dependent, in turn, on other aspects of the accident, as well as the geometry of the reactor. Because of this, metal-water and associated chemical reactions in reactor accidents should not be treated in a compartment by themselves but should be considered in relation to the many factors present. Only in considering an integral model of the reactor during an accident can the role of the chemical reactions be assessed realistically.

1.3.2 Reactor Accidents Having the Necessary Conditions for the Metal-Water Reaction

Because the rate of the metal-water reaction is very dependent on temperature, one or both of two events must occur in a nuclear reactor before this reaction is very significant. Either the heat-generation rates in the core must increase to values higher than normal and/or the heat-removal rates in the core must decrease to values lower than normal. Engineered safety features incorporated in the reactors probably would limit these changes in case of an accident to a range such that the rate and extent of the metal-water reaction would be small or negligible. In the very improbable case of these safety features failing during the accident, one or both these changes could be significant in the following situations:

1. nuclear excursion accident,
2. loss-of-coolant accident,
3. loss-of-flow accident,
4. loss-of-pressure accident.

A simplified sequence diagram of the first two accidents for the case without engineered safety features is shown in Fig. 1.1; this diagram puts the metal-water reaction in perspective with the other aspects of the accidents. It can be seen that the chemical reaction is not the initiating mechanism, but it does increase the possibility and somewhat

Fig. 1.1. Simplified Accident-Sequence Diagram for Reactors Without Engineered Safety Features.

shorten the time required for the radioactive materials to reach the reactor site environs.

In a nuclear excursion accident, heat-generation rates in the reactor core are higher than normal because of the insertion of additional reactivity. Energy is deposited at a very rapid rate in the fuel, but it is deposited at a somewhat slower rate in the cladding because of the relatively high thermal lag in the UO_2 fuel. If the magnitude of the excursion were large, melting, fragmentation, or even vaporization of part of the core could take place. Normally the engineered safety features incorporated in these reactors will prevent excursions of this magnitude. These features include devices such as controls to limit the worth of any given control rod, putting massive support structures under the control rod drives, having rapid scram action, and designing the control rods so that they cannot be removed from the core rapidly. Also it is fortunate that the fuel Doppler coefficient in light-water power reactors is high, and advantage of

this inherent behavior is taken in calculating the limit of these excursions. By limiting the extent of the nuclear power bursts, the extent of the metal-water reaction is usually small. However, if the pessimistic assumption is made that these safety features may not operate properly, the possibility that the metal-water reaction may take place must be accepted. Associated with the accident in this extreme case would be the possibility of steam explosions and water hammers that could threaten the integrity of the reactor vessel and the primary cooling system.

For the loss-of-coolant accident, heat removal rates in the reactor core are lower than normal due to the loss of the primary cooling water. This accident is generally considered to be initiated either by a pipe break in the primary coolant system or by a rupture of the pressure vessel. The latter mechanism, however, is considered to be incredible in reactor safety analyses (Refs. 36, 37).^{*} With the occurrence of a pipe break, the primary coolant will be discharged from the reactor system and the reactor will become subcritical by void formation and/or control rod insertion. The reactor core will heat up because of the fissions due to the delayed neutrons, the decay of the fission products, and the exothermic metal-water reaction. The metal-water reaction results from the hot core metal coming in contact with steam, which could be formed by the boiling of the water remaining in the bottom of the pressure vessel after the coolant blowdown and would flow upward through the core region. Normally an emergency core-cooling system would be activated upon the loss of the coolant, and its effect would be to limit the core heatup so that there would be little or no metal-water reaction. Such emergency core-cooling systems spray and/or flood the reactor core with water; they are discussed in detail by Lawson.²

If the pessimistic assumption is made that the emergency core-cooling systems are inoperative, it must also be assumed that there will

^{*}This assumption has been questioned; see letter from W. D. Manly, Advisory Committee on Reactor Safeguards, to G. T. Seaborg, USAEC, Nov. 24, 1965; included in USAEC Press Release, H-262, Dec. 3, 1965.

be significant metal-water reaction. Eventually the core melting temperatures will be reached, and fuel assemblies will slump and fall to the bottom of the pressure vessel. Constituents of the molten fuel assemblies may then be expected to penetrate the vessel, but the nature or the state of this molten material before and after it penetrates is uncertain. However, it is possible for steam explosions to occur and for the molten core material to continue to react with any water left in the pressure vessel or the containment vessel. Further, it can be argued that for this extreme case the containment vessel could fail by any one of a number of mechanisms, such as the generation of shock waves, buildup of hydrogen pressure due to the metal-water reaction taking place for long periods of time, or the melting and breaking apart of the containment vessel material.

Hydrogen can be produced in a loss-of-coolant accident by the metal-water reaction and/or radiolysis of the water from the emergency core-cooling systems. For power-reactor safety analyses,³⁶⁻³⁷ it is generally assumed that this hydrogen is always below its flammable limit or that it burns in the containment vessel. There is some question about hydrogen pocketing in the containment vessel and forming a mixture that could detonate. To eliminate this possibility, it has been often suggested or even required that the containment vessel be filled with nitrogen to provide an inert atmosphere. However, all reactor manufacturers generally argue strongly against this because it makes personnel access to these vessels more difficult and expensive. They feel that the overall situation is less safe because of the increased difficulty in inspecting and maintaining equipment within the containment vessels.

Finally, for both the loss-of-flow and loss-of-pressure accidents, the heat-removal rates in the core would be lower than normal, but the water would remain in the reactor primary coolant system. The core heatup in a loss-of-flow accident could be limited by protective devices designed for the loss-of-coolant accident. Therefore the consequences from this type of accident are not considered to be so severe as those from the loss-of-coolant accident. For the loss-of-pressure accident, the flow system would still be operable at atmospheric pressure, and this would be sufficient to remove the afterheat from the reactor core.

1.4 Summary of Findings of this Review

This review of the status of potential chemical reactions in various hypothetical accidents in light-water power reactors indicates that the rates and the extents of these reactions are very dependent on the accident definition. They must be considered as only one of the many aspects of the accident, and only by considering integral models of the accident can the consequences of the chemical reactions be assessed realistically. The uncertainties connected with the definition of the accident and its mathematical simulation are much greater than those connected with the basic kinetics of these reactions. Therefore, for engineering purposes, the basic rates of the metal-water reaction are defined sufficiently well. Much is known about the reaction with air of the hydrogen produced by the metal-water reaction, although the detonation limits of hydrogen-air-steam mixtures and the possible pocketing are not well defined.

1.4.1 Reactions of Zirconium and Zircaloy with Water

Much of the study of the metal-water reaction has been devoted to zirconium and its alloys because of the almost universal use of this material as fuel cladding in light-water power reactors. The mechanism of this reaction is believed to be the formation of oxygen ion vacancies in the metal and at the metal-oxide interface.³⁸⁻⁴⁰ When there is excess steam available at the metal's surface, the most accepted relation describing the reaction rate between zirconium and steam is that derived by Baker and Just,⁴¹ which is

$$w^2 = 33.3 \times 10^6 t \exp \left(\frac{-45,500}{RT} \right),$$

where w is weight (mg) of zirconium reacted per unit (cm^2) of surface area, t is time (sec), R is the gas constant ($1.987 \text{ cal/mole} \cdot ^\circ\text{K}$), and T is temperature ($^\circ\text{K}$). In this form of the correlation, it is tacitly assumed that all the reacted metal is converted into stoichiometric ZrO_2 , but this is a simplification of the situation. Actually some of the oxygen from the steam forms a solid solution and lesser oxides, such

as $\text{ZrO}_{1.97}$, with the zirconium. However, in accident analyses, the error introduced by the assumption of the formation of the stoichiometric oxide is small compared with the other assumptions commonly used in these analyses. This is verified by the fact the zirconium-steam reactions in the condenser discharge experiments, in the experiments with fuel-pin samples heated in an electrical furnace, and in the experiments with fuel-pin samples heated by induction could be explained by this relation:

$$w^2 = 5.77 \times 10^6 t \exp \left(\frac{-40,500}{RT} \right) \dots$$

However, the differences between this and Baker and Just's relation are small. Samples of zirconium heated in air show a greater rate of weight gain than samples heated in steam because zirconium reacts with the nitrogen in addition to the oxygen in the air.²⁶

Tests of Zircaloy-clad UO_2 fuel-pin specimens heated by induction to melting or slightly below melting temperatures and subsequently cooled by a water spray indicate that such assemblies could be cooled effectively under loss-of-coolant accident conditions.⁴² However, these specimens became very brittle and fragmented prior to or during the dismantling of the experimental assemblies. The problem this suggests is that there might be collapse of a sufficient amount of the reactor core that it could not be cooled effectively by the emergency core-cooling system. The fragmentation appears to have been due to the metal-water reaction that occurred,⁴³ although it is recognized that the temperature-time history of the specimens and the oxidation of the cladding were not independent of each other. Certainly this needs further investigation.

During the heatup of the fuel pins in a loss-of-coolant accident, it is likely that many will rupture because of the high internal pressures due to the fission products and the low tensile strength of Zircaloy at high temperatures. Tests^{26,44,45} of "fresh" Zircaloy tubing and Zircaloy-clad UO_2 specimens indicate that the mode of failure is the swelling (bulging) of the cladding with the formation of a small longitudinal crack at hoop stresses corresponding to the ultimate

tensile strength of the metal. This indicates that there would be no gross movement of the UO_2 fuel within the reactor core as a direct result of this type of failure. However, it may be possible that this swelling could interfere with the flow of steam in the reactor core, which would influence the nature of the metal-water reaction and any core disassembly. Also it could interfere with the effectiveness of the emergency core-cooling systems. (Reference is made to Lawson's report² for a further discussion of this subject.) Additional tests have been started with Zircaloy tubes in a steam atmosphere and with Zircaloy tubes that have seen reactor service. Preliminary results from the tests in steam atmospheres indicate that there is less swelling of the cladding and that the cracks are a little more brittle in nature.

The nature of the meltdown of Zircaloy-clad fuel pins under loss-of-coolant accident conditions without emergency core cooling is not well understood.¹ In an inert atmosphere, molten Zircaloy appears to have a low viscosity, but it seems to be quite viscous in a steam atmosphere.^{42,46} Specimens heated to 2140°C in a steam atmosphere showed evidence of local melting and some interaction between the UO_2 fuel and the Zircaloy cladding, but there was no evidence of molten Zircaloy running down the side or dripping away from the fuel pin. Other tests^{17,47} with preoxidized fuel-pin specimens in an inert atmosphere indicate that the cladding started to fail at the melting point of the Zircaloy but that the oxide tended to retain the molten material. As the temperature increased, the molten zirconium tended to dissolve this oxide and to wash the UO_2 fuel. TREAT "flat-top transient" experiments⁴⁸ in which fuel pins suspended over a pool of water were melted by fission energy indicate that the metal-water reaction for the meltdown situation is between 32 and 44% and that there are no sudden pressure surges when the molten fuel falls into the pool of water.

TREAT studies⁴⁹⁻⁵² indicate also that there is negligible metal-water reaction during a nuclear excursion until the fuel starts to melt, which is equivalent to a peak fuel enthalpy of about $220 \text{ cal/g } \text{UO}_2$. The extent of the metal-water reaction then increases linearly with additional

fission energy input to the fuel. These studies also show that the fuel pin remains essentially intact until the fuel is completely molten, which is equivalent to a peak fuel enthalpy of about 280 cal/g UO_2 . In understanding these data for their application to hypothetical accident situations, the modes of conversion of the fission-energy input to the fuel pins to mechanical energy and the subsequent dissipation of this mechanical energy need to be known. Photographic studies in TREAT⁵³ and additional tests in the CDC-PBF program,^{54,55} along with the appropriate analytical studies, have been initiated to delineate the nuclear excursion accident conditions more fully. The effects of the reactor period, the coolant conditions, and the fuel-pin geometry are being considered. Preliminary results from these studies indicate that the contribution of the metal-water reaction to the potential consequences of a nuclear excursion, such as the breaking apart of the reactor core and the possible rupture of the primary coolant system, is small.

1.4.2 Reaction of Stainless Steel with Water

Although stainless steel is rarely considered now for use as a fuel cladding material in light-water power reactors, it is used in some of the existing reactor cores. Stainless steel reacts very little with steam at temperatures below its melting temperature ($\sim 1400^\circ\text{C}$) until its temperature is greater than about 1000°C . Reaction rates that have been measured so far for stainless steel samples at temperatures between 1000 and 1400°C appear to be dependent on factors such as the sample heatup rate.^{17,56-59} Because of this, there are some differences in the reaction rates reported in the literature. However, White¹⁷ was able to correlate the results of his experiments for the reaction rate of stainless steel with steam for the time following an initial period of 6 to 28 min by the following equation:

$$w^2 = 2.4 \times 10^{12} t \exp\left(\frac{-84,300}{RT}\right),$$

where w is oxygen uptake (mg) per unit (cm^2) of stainless steel surface area, t is time (sec), R is the gas constant ($1.987 \text{ cal/mole}\cdot^\circ\text{K}$), and

T is the temperature ($^{\circ}\text{K}$). During the initial period of 6 to 28 min, White found the reaction rates to be linear. White's equation indicates that for temperatures above 1200°C , the rate of oxygen uptake from steam per unit surface area of the stainless steel is greater than that for zirconium.

As stainless steel reaches its melting temperature in steam, it tends to foam or bloat, and it is extremely difficult to define the surface area available for the reaction. However, experiments by Wilson and his associates²⁰ that simulated a stainless steel-clad UO_2 fuel pin in loss-of-coolant accident conditions indicate that a good assumption for the reaction rate is that the stainless steel is unreactive until it reaches its melting temperature. As the stainless steel reaches this temperature, it is assumed then that it reacts with all the available steam until it is consumed. Multipin experiments indicated that the foam-like material produced at temperatures above 1400°C bridged the coolant channel in some cases. However, it did not seem to interfere with the steam flow in these particular experiments. Also at these higher temperatures, the formation of eutectics between the stainless steel oxides and the UO_2 fuel has been observed. The exact meltdown mechanism of stainless steel-clad UO_2 fuel pins is uncertain, but it appears that stainless steel oxides melt in the range 1450 to 1600°C and form a viscous material that slumps away from the fuel. There also appears to be some removal of the UO_2 fuel because of the eutectic formation.

The product of the stainless steel-steam reaction appears primarily to be a spinel-type compound, such as Fe_3O_4 . Samples that have reacted for long periods of time have Fe_2O_3 on the outer surface and FeO next to the metal, but most of the product is Fe_3O_4 . The heat of this reaction was calculated to be 155 cal/g of stainless steel based on the Fe_3O_4 product.

TREAT experiments^{49-51, 53} indicate that the situation in nuclear excursions for the stainless steel-clad UO_2 fuel pins is similar to that for the Zircaloy-clad UO_2 fuel pins. There is negligible metal-water reaction until the fuel starts to melt (a fuel enthalpy of $220 \text{ cal/g } \text{UO}_2$).

The extent of the metal-water reaction increases linearly for fuel fission-energy inputs greater than this value, although the amounts for stainless steel for a given fission-energy input are not so great as those for zirconium. Also, for the stainless steel-clad fuel pins, there is little fragmentation until nearly all the fuel has become molten. Therefore for this situation too, the metal-water reaction appears to be a small factor in determining the consequences of a nuclear excursion accident. The stainless steel fuel pins also have been included in the TREAT photographic studies⁴³ and the CDC-PBF tests^{54,55} initiated recently to study the nuclear excursion accident conditions more fully.

1.4.3 Reaction of Aluminum with Water

The review of the metal-water reaction for aluminum is limited to this metal's behavior in nuclear excursions, since aluminum is not used in large light-water power reactors. However, the only reactors that have had destructive nuclear excursions are those with aluminum-uranium alloy fuel plates. The TREAT studies^{8,60} indicate that there is little metal-water reaction until the fission-energy input to the fuel-plate samples is greater than about 350 cal/g. When the metal temperature reaches 1400°C, there are indications that vaporization of the aluminum takes place and there is a rapid increase in the extent of the metal-water reaction. TREAT photographic studies⁶¹ indicate that fuel-plate specimens containing the uranium-aluminum alloy do not fragment until after the fuel plate has ignited. Some tests in which molten aluminum was allowed to come into contact with water resulted in some very large pressure pulses.⁶²⁻⁶⁵ However, the contribution of the metal-water reaction to these pulses appears to be negligible. The mechanism of the generation of these pulses (steam explosions) is very complicated and should be investigated further.

1.4.4 Reaction of UO₂ with Water

Uranium dioxide can react with steam to form higher oxides, such as UO_{2.27} at 1000°C or UO_{2.17} at 1600°C. However, the presence of hydrogen,

such as that generated by the metal-water reaction of the cladding, greatly inhibits this reaction. Also the amount of heat generated by this reaction is negligible. (This reaction possibly could be slightly endothermic in some cases.) The reaction rate during the initial period of the oxidation of UO_2 by steam has been correlated by White¹⁷ to be

$$w^2 = 1.65 \times 10^5 t \exp \left(\frac{-50,800}{RT} \right),$$

where w is oxygen absorbed (mg) per unit (cm^2) of surface area, t is time (sec), R is the gas constant (1.987 cal/mole $\cdot^\circ\text{K}$), and T is temperature ($^\circ\text{K}$). Tests involving the dropping of molten UO_2 into water indicate limited chemical reaction, with the end product being very friable and easily broken into a coarse powder.⁶⁶

1.4.5 Other Chemical Reactions

Several miscellaneous chemical reactions considered in accident analysis work were reviewed. Most of these reactions are not exothermic, but they have a bearing on the nature of fragmentation and meltdown of a reactor core of the type that could occur for the very degenerate case of a loss-of-coolant accident without emergency core cooling. Since the interest in this situation is not nearly so great as for situations with emergency core cooling, work on these reactions is much more limited.¹

There has been evidence of reduction of UO_2 by zirconium,⁵⁶ and some data for the rate of this reaction for temperatures below 1100°C have been reported.^{67,68} Work has been done on the ternary phase diagram for mixtures of zirconium, uranium, and oxygen, but it is rather limited.⁶⁹ Interaction between molten zirconium and stainless steel is not understood completely, but the iron-zirconium phase diagram⁷⁰ indicates that eutectics with melting points as low as 934°C can be formed. More work in this field is suggested.

Although the formation of eutectics between stainless steel oxides and UO_2 fuel has been observed,²³ definitive data on these eutectics are lacking. Some preliminary tests of such mixtures indicate that their

melting points in air approach those of the stainless steel oxides.²² In preliminary tests of materials often suggested for "molten core catchers," several showed good resistance to penetration by molten UO_2 , but only graphite showed no signs of chemical attack.⁷¹ However, it should be remembered that the hot UO_2 could heat the graphite to temperatures at which it would react easily with the surrounding air.

It is conceivable that in a reactor accident the stainless steel sheathing for the absorbing materials in the control rods can become damaged and expose the absorbing materials. Boron carbide reacts with air or steam at temperatures greater than 450°C to form a B_2O_3 oxidation product, as well as volatile boric acid.⁷² Little information appears to be available regarding chemical reactions of silver-cadmium-indium alloys, but it appears⁷³ that the alloy would simply flow out of the ruptured control rod sheath after it had reached its melting point of 775 to 826°C .

There is some concern that hot zirconium will absorb hydrogen from steam-depleted gas streams. The hydrogen-zirconium phase diagram indicates that hydrogen is soluble in zirconium at temperatures greater than 1000°C , but high pressures are required.^{29,30,31,33} Also it is known that small amounts of water vapor in the gas stream and the presence of oxide on the zirconium metal surface will greatly reduce hydrogen absorption by the metal.¹⁹

1.4.6 Reaction of Hydrogen with Air

The information available on hydrogen-air reactions was not reviewed in complete detail, but it was reviewed sufficiently to obtain some idea of the nature of the reaction and to indicate some of the unknowns. Flammability and detonation limits of hydrogen-steam-air mixtures most often referenced in reactor safety analyses are those reported by Shapiro and Moffette.⁷⁴ These limits are based for the most part on the works of Zabetakis^{75,76} and Coward and Jones.⁷⁷ Actually these limits are a simplification of a very complicated process, since the hydrogen-air reaction is made up of several reactions.^{78,79} Therefore these limits can be influenced by several variables, such as

pressure, temperature, size of the containing vessel, and the direction of the burning flame. It has been calculated that nitrogen and, more particularly, water vapor are effective in reducing the detonation limits of these mixtures.^{80,81} However, experimental verification of these limits, particularly those for hydrogen-steam-air mixtures, are lacking.

Spontaneous ignition temperatures of hydrogen-steam-air mixtures have been calculated from data of small-scale experiments with hydrogen-oxygen mixtures.^{80,81} These calculations indicate that an increase in the vessel size decreases these temperatures, while nitrogen diluent and, more effectively, water-vapor diluent increase them. Again experimental verification of these calculations is limited to some values reported by Shapiro and Moffette.⁷⁴ Spontaneous ignition temperatures of hydrogen-steam mixtures flowing out of a pipe into air have been measured to be between 680 and 835°C. Placing an object in front of the hydrogen-steam nozzle reduces this temperature to about 520°C, which is about the same as that for a static system.

Production of hydrogen by the radiolytic decomposition of water has been of concern in reactor safety. This subject has been discussed in several references.⁸²⁻⁸⁴

1.4.7 Analyses of the Metal-Water Reaction in Nuclear Excursion Accidents

The primary concern with regard to nuclear excursions in reactors is that they could possibly result in damage to the core such that it could not be cooled after the excursion and/or they could rupture the primary coolant system (additional damage in case of the rod-ejection accident). Analyses of the nuclear excursion accident in power reactor safety analysis reports try to show that the nuclear excursion does not result in these consequences.

Water-moderated and -cooled reactors that have had destructive nuclear excursions are limited to those that were small compared with present-day power reactors and had plate-type fuel elements consisting of highly enriched uranium-aluminum alloy with aluminum cladding.

Because of these differences, extrapolation of the data from these excursions to power reactor situations must be done with care. Metal-water reaction was observed in all excursions, and comparisons with the amount of the reacted metal found in the debris and that predicted by calculations based on the TREAT data are good.⁸ Analyses of the pressure pulses that occurred during these excursions are very complex and are still under development.^{63,65,85} However, it appears that these pulses were due primarily to the rate of heat transfer from the fuel to the coolant (transient boiling), and the metal-water reaction contributed little to them.

By incorporating appropriate engineered safety features in the design of power reactors and taking advantage of the high Doppler coefficient for slightly enriched UO_2 fuel, the extent of any nuclear excursion is limited to values below which the damages described above could not occur. The fission-energy inputs to the fuel during the excursion are calculated from models based on the nondestructive excursion tests of the SPERT I reactor with an oxide core.^{86,87} Knowing these fission energy inputs, the peak fuel enthalpy values are calculated and the fuel-pin behavior is predicted from the results of TREAT and other experiments. In most situations, the worst excursion is limited to reactivity inputs such that the maximum fuel enthalpy is less than 280 cal/g UO_2 . The TREAT data indicate that all the fuel does not melt and the fuel pins do not fragment until this enthalpy value is reached. This limits the area available for heat transfer, and then it is possible to calculate that the pressure surges resulting from these nuclear excursions are within acceptable limits. The metal-water reaction is limited and plays a very minor role in these situations.

Nuclear excursions that result in maximum fuel enthalpies greater than 280 cal/g UO_2 generally cause the fragmentation of the fuel pins. In this case, the consequences of the accident are more difficult to define and simulate mathematically.^{65,85,88} Conversion of the thermal energy into mechanical energy and the dissipation of this mechanical energy in the reactor system must be considered. Both are very complex subjects, but much has been done with them. Although there is metal-water reaction in these cases, it appears that the reaction contributes

little to the destructive mechanism of a nuclear excursion. This is the case because the integrated fission energy generated during the excursion is much greater than the metal-water reaction energy, and the rates of the metal-water reaction are slow compared with those of the other events that take place during the excursion.

The reactor manufacturers state that for excursions resulting in peak fuel enthalpies greater than 280 cal/g UO_2 (the fuel pins fragment) but less than 360 cal/g UO_2 (UO_2 does not vaporize), there would be no extensive damage to the reactor core or to the remaining primary coolant system. Here again the contribution of the metal-water reaction to the consequences of the accident appears to be small. In the case of the BWR's^{89,90} the worst excursion occurs for a free fall of a control rod from a just-critical reactor core. If the rods are withdrawn in the specified sequence, the maximum fuel enthalpy during the power burst is less than 280 cal/g UO_2 , which is below the enthalpy at which the fuel pins could fragment. However, if the rods are withdrawn out of sequence (overriding the action of the control rod minimizer), the peak fuel enthalpy is about 330 cal/g UO_2 . General Electric states that peak fuel enthalpies as high as 360 cal/g UO_2 (UO_2 vapor pressure is 1 atm) could be tolerated in a nuclear excursion.⁸⁹ For the PWR's, the worst excursion occurs when a control rod is ejected from the reactor vessel.⁹¹⁻⁹⁴ Analyses of this accident by all the PWR vendors so far indicate that the maximum fuel enthalpy is always below 280 cal/g UO_2 (in some cases it was predicted that no fuel would melt). Both Westinghouse³⁴ and Combustion Engineering⁹⁵ have made some preliminary calculations which indicate that maximum fuel enthalpies of greater than 280 cal/g UO_2 in a nuclear excursion accident could be tolerated. Only Babcock & Wilcox⁹³ calculated a significant portion of the energy released during the nuclear excursion to be from the metal-water reaction. This appears, however, to be more due to the conservative way the metal-water data were handled in their calculations than would be the case for the actual situation.

More work is needed to determine the effects of the nuclear excursion when the fission-energy input to the fuel pins results in peak fuel

enthalpies greater than 280 cal/g UO_2 . For example, Ivins⁴³ demonstrated that a severe pressure pulse was produced when the fuel pin was subjected to a fission energy input of 360 cal/g UO_2 . As mentioned earlier, such factors as the neutron flux depression in the fuel, reactor period, and the state of the water surrounding the fuel pin may be important. Such studies have been started in the TREAT⁴³ and CDC-PBF programs.⁵⁵

1.4.8 Analyses of the Metal-Water Reaction in Loss-of-Coolant Accidents

In the case of loss-of-coolant accidents, use of the criterion of no cladding melting for the emergency core-cooling systems limits the extent of metal-water reaction in power reactors to less than 1% (Refs. 37, 91, 96-99). Without the use of a core-cooling system, the extent of the metal-water reaction would, of course, be much higher. Therefore the time required for the emergency core-cooling system to start operating is important with regard to the extent of the metal-water reaction that could take place in a loss-of-coolant accident. The possibility of the metal-water reaction causing fragmentation of the cladding^{42,43} makes it difficult to interpret quantitatively the criterion that the cladding metal-water reaction is to be limited to negligible amounts. If a sufficient amount of the core fragmented, the effectiveness of the emergency core-cooling systems in cooling the core would be questionable. Certainly more work is needed in this area.

Since the rate and the extent of the metal-water reaction is very dependent on the cladding temperature and the steam availability to the metal surface, the geometry of the reactor is very important. The steam is generally thought of as evolving from the boiling of the water remaining in the pressure vessel following the coolant blowdown. In many cases, the rate and the extent of the metal-water reaction are limited by the amount of steam that reaches the cladding surface. (It is conceivable that a partially operating emergency core-cooling system can furnish additional steam for the metal-water reaction. However, as will be seen later, reactor vendors generally assume that unlimited steam is available for the metal-water reaction in the design of their

emergency core-cooling systems.) Much analytical and experimental effort has been directed toward finding methods of predicting coolant behavior during blowdown.^{100,101} Although methods have evolved to the point where they predict the pressure behavior in the reactor system with reasonable accuracy, the amount of water predicted by them to be left in the pressure vessel tend to be low.

The state of the reactor core at the end of blowdown influences greatly the temperature-time history of the cladding during the core heatup period, which also influences greatly the rate of the metal-water reaction. Experiments and calculations indicate that there will be little structural damage to the core during blowdown.¹⁰² However, the transient heat transfer coefficients during blowdown have a great bearing on the temperature distribution in the core at the end of blowdown.¹⁰³ Values of the blowdown heat transfer coefficients reported in the literature are limited to those reported by General Electric.¹⁰⁴ More work should be directed to obtaining better blowdown heat transfer coefficients because of their importance to core heatup and subsequent metal-water reaction.

The heat required to boil the water remaining in the bottom of the pressure vessel is usually assumed to be the sensible heat in the pressure vessel's wall and heat radiating from the bottom of the reactor core.¹⁰⁵⁻¹⁰⁷ Some calculations have indicated that the contribution of heat from the latter source is negligible for at least the first 500 sec of the accident.¹⁰⁵ Recognizing the limitations of the calculations for predicting the amount of water left in the pressure vessel, the general consensus of the present investigators is that the initial boiloff rates of the water remaining in the vessel normalized to the vessel's cross-sectional area are the same for all power and LOFT reactors. However, the rate of decrease of the boiloff is greater for the thinner wall vessels; hence it will be the greatest for LOFT and the least for the large PWR's. Therefore, the metal-water reaction is indirectly dependent on the pressure vessel wall thickness.

A number of computer programs have been developed to describe core heatup, including the effects of the metal-water reaction, following coolant blowdown.^{1,101} These programs vary some in their complexity,

but the assumptions used in them are based on the experimental information available at the time the programs were written. Prior to meltdown, it is assumed that the fuel pins remain in their original configuration. The recent experiments and calculations of the fission-gas pressure inside the fuel pins and the tensile strength of Zircaloy indicate that breaks in the cladding will be relatively small and that there will be no gross movement of the UO_2 fuel. The effect of the swelling of the cladding during this period on the effectiveness of the emergency core-cooling systems is beyond the scope of this report and is discussed by Lawson.² Also it appears that the swelling would have little influence on the extent of the metal-water reaction unless of course it greatly interfered with the steam flow in the reactor core. However, these results and the possible fragmentation of the cladding even without any melting, as described earlier, suggest that the assumption of the original pin geometry be examined further.

When there is excess steam available to the cladding surface, the rate of the metal-water reaction is described by Baker and Just's parabolic relation⁴¹ in all these programs. With the exception of General Electric's TACT-V program,¹⁰⁴ all these programs have a provision for assuming that the metal-water reaction is limited by the amount of steam flowing through the reactor core. In the case where the emergency core-cooling system cools the core following a break in the primary coolant system, the extent of the metal-water reaction is very limited, and it can be described adequately by Baker and Just's relation. This relation shows that the metal-water reaction is negligible until the cladding surface reaches 1000°C . Results from these heatup programs also indicate that the hot-spot temperature in the core up to 1000°C can be described adequately by an adiabatic heatup model.¹⁰⁸ For the case without effective action of the emergency core-cooling systems, the rate of the metal-water reaction is limited by the amount of steam flowing through the core.^{103,109} As a result, the cladding in the core would not be ignited by the metal-water reaction. Some of the computer programs^{105,110} take into account additional resistance of the diffusion of steam through the hydrogen-rich film adjacent to the metal

surface in calculating the rate of the metal-water reaction. However, it appears that the effect of this added resistance is small.

Results of studies made with the heatup programs for the various reactors indicated that the rate and extent of the metal-water reaction are sensitive to the reactor power density, the length of the fuel pins, the heat transfer coefficient from the fuel pins to the fluid flowing through the core, and the initiation time for operation of the emergency core-cooling systems.^{107,108,111,112} The reactors with the higher power densities have greater percentages of the cladding reacting. Also the reactors with the shorter fuel pins have greater percentages of the cladding reacting, since about all the steam flowing into the core is consumed in the lower part of the core. This starves the upper part of the core of any steam and usually results in the peak fuel temperatures and the first melting of the cladding being located at some position below the core midplane. It should be pointed out that although the PWR's have higher initial overall metal-water reaction rates than the BWR's because of their higher power densities, the overall reaction rates are about the same for both reactor types after the first 80 sec because of the steam supply limitations. The distribution of the power density within the core greatly influences the local metal-water reaction within the core, but it has little influence on the overall rate of reaction for the entire core. These analyses also showed that the factors having little effect on the rate and extent of the metal-water reaction are the reactor power level, the emissivity of the cladding, the temperature of the water from the emergency core-cooling systems, and the heat necessary to heat the steam to the reaction temperature at the site of the reaction. Any variation in the exponential activation energy constant in the parabolic relation describing the metal-water reaction results in a significant change in the rate of this reaction in the reactor core, but variations in the linear diffusion constant in this relation have little effect.¹¹²

Some simplified calculations made for the LOFT core with stainless steel cladding instead of Zircaloy cladding indicate that the overall

extent of the metal-water reaction is not so great for stainless steel.¹¹³ This is primarily due to the lower heat of reaction for the stainless steel-water reaction.

The metal-water reaction during and following the very unlikely event of meltdown of the fuel pins is not known very well because it is dependent on the core geometrical behavior, which is subject to much speculation and conjecture.¹ Many factors, such as the structural and control rod heat sinks in and surrounding the core, influence this meltdown behavior.^{103,105,110} For the double-ended failure of the largest pipe (recirculation line for the BWR's) in the primary coolant system of a power reactor, it is believed that the cladding will start to melt about 50 to 100 sec after the initiation of the accident if the emergency core-cooling system does not operate.

Significant quantities of core debris could accumulate in the bottom of the pressure vessel in about 10 to 60 min, and it would probably melt through this vessel in about another 20 to 60 min. Metal in contact with the water or steam would continue to react and there could be steam explosions during this process. The subject of steam explosions is very complex and needs more investigation, but it appears that the metal-water chemical reaction contributes little to them.^{43,62,114} There is the potential of the molten core material to react with any water or steam adjacent to it for long periods of time and generate sufficient hydrogen to rupture the containment vessel.

Because of the many uncertainties regarding the meltdown behavior of the reactor core, calculational models used to predict the metal-water reaction during this period have many gross assumptions. However, they do indicate that the extent of the metal-water reaction of the cladding by the time the core has melted is between 25 and 50%. Core heatup programs incorporating more sophisticated meltdown models indicate that this value could be less.^{105,107} A better definition of the core meltdown behavior would be required to obtain a more accurate value. This would require extensive experimentation, and the cost and diversion of manpower and resources for such a large program should be weighed against the potential benefits.¹

Recognizing the possible problem of hydrogen absorption in the upper part of the reactor core, as discussed earlier, hydrogen produced by the metal-water reaction is usually assumed in accident analyses to pass out of the primary coolant system into the containment vessel. At this point it is assumed further that the hydrogen either burns or it is below its flammable limit. As was mentioned earlier, there are uncertainties associated with the flammable and the detonation limits, as well as with the spontaneous ignition temperatures, but there are many more uncertainties with the accident definition,^{80,103} and it may be such that the double-ended failure of the largest pipe in the primary coolant system is not the worst case from the viewpoint of the hydrogen-air reaction. Another source of hydrogen in a loss-of-coolant accident is that produced by the radiolytic decomposition of the water from the emergency core-cooling systems.

One of the main uncertainties regarding hydrogen in a loss-of-coolant accident is the possibility of it pocketing within the containment vessel. This apparently did occur and cause an explosion in the EBR-II air lock.⁴³ The factors that cause hydrogen to pocket within the containment vessel are its bouyancy due to its lower molecular weight and its possible higher temperature. Factors that cause it to mix with the other gases are molecular diffusion and natural and forced convection. These should be investigated further. If the hydrogen does burn as it leaves the primary cooling system, flames as long as 20 ft could be produced that could impinge on the surrounding reactor structures.¹⁰³

It has been suggested often that the containment vessel be filled with nitrogen to provide an inert atmosphere and thus prevent the hydrogen-air reaction. In general, reactor manufacturers are very much opposed to this. They feel that this would result in a less safe overall situation, since inspection and maintenance on the components within the vessel would be less frequent because of the difficulty of access. General Electric is making provisions to fill the BWR drywells with nitrogen but is very much against activating these systems.^{115,116}

2. NATURE OF METAL-WATER AND ASSOCIATED REACTIONS

The available experimental information on basic metal-water and other chemical reactions that could possibly take place during a reactor accident is reviewed in this chapter. Data from experiments with fuel-pin specimens heated electrically or by fission energy are considered. The application of these data in reactor accident analyses, as well as experiments relating to these applications, are described in the next chapter. Experiments in which the metal-water reaction is being studied cover a spectrum of sizes and complexity. Because of this, the division between the experiments described in this chapter and those described in the next chapter is somewhat arbitrary. Many of the USAEC-sponsored projects that include these experiments are summarized in the draft of the summary description report prepared by the Water-Reactor Safety Program Office.³

Much of the recent work on the metal-water reaction has been directed to zirconium and its alloys because of its extensive use as a cladding material in power reactors. As a result much literature regarding this subject has been published, and a considerable portion of this chapter is devoted to reviewing it. The reactions of stainless steel and aluminum with water and/or steam also have received much attention because of their use in nuclear reactors. The review of the metal-water reaction for aluminum is limited here, however, to nuclear excursion investigations and the studies of the impact of water on molten aluminum. This limitation is made because aluminum is not a common material in light-water power reactors, but the only reactors of interest that have had destructive nuclear excursions are those with aluminum-uranium alloy fuel plates. In the case of the hydrogen-air reaction, this review is limited because of the extensive amount of literature on this subject and limited time available for this study. However, this reaction was reviewed sufficiently to identify some of its uncertainties.

2.1 Reaction of Zirconium or Zircaloy with Water

2.1.1 Recent Summaries

As mentioned above, the reactions of zirconium and its alloys with water or steam have been studied extensively. Several review articles on these reactions have been written, and the more recent of these are the ones by Baker and his co-workers,^{8,9,60} Morrison and his associates,^{105,117} and White.^{16,17,47} Although there may be some minor variations in the different correlations, these reviewers all agree that the reactions of solid zirconium and its alloys with water and/or steam are known well enough for application in reactor accident analyses.

2.1.2 Physical Chemistry of the Reaction

If there is an excessive quantity of steam or water surrounding the solid metal, the absorption of oxygen by the zirconium is controlled either by (1) the gaseous diffusion of steam to the solid boundary or (2) the diffusion of the oxygen ions through the oxide film and into the base metal.^{41,105,117} The former mechanism is the controlling factor for a fresh metal surface that reacts immediately with any water vapor reaching the solid surface. For the reaction to continue, the water vapor must diffuse through a film that is rich in the hydrogen formed by the metal-water reaction. However, as the metal surface becomes oxidized, the oxide film creates an additional resistance and eventually becomes the limiting factor in the rate of the metal-water reaction.

The mechanism of the solid-state process has been studied by Lustman¹¹⁸ and by Pemsler.³⁸⁻⁴⁰ Two different phenomena take place during this process: (1) the formation of a zirconium-oxygen solid solution and (2) the formation of the oxide of zirconium. These processes are illustrated in Figs. 2.1 and 2.2. Figure 2.1 shows a Zircaloy-4 sample containing both zirconium-oxygen solid solution and zirconium oxide. Figure 2.2 shows another typical Zircaloy-4 sample and more detail of the oxide phase. A slightly substoichiometric oxide ($\sim \text{ZrO}_{1.97}$) is located between the stoichiometric oxide and the

Fig. 2.1. Zircaloy-4 After Heating at 3.0°C/sec to 1600°C in Steam.
(From Ref. 17)

Fig. 2.2. Zircaloy-4 After Heating at 0.3°C/sec to 1300°C in Steam.
(From Ref. 16)

zirconium metal. This phase has the same crystal structure as the stoichiometric oxide, but it has a black instead of a white color, and the alloying tin metal in this phase does not appear to be oxidized.¹⁸ Both the solid-solution and reaction processes are thought to be due to the formation of oxygen ion vacancies in the metal and at the metal-oxide interface. These vacancies, along with the zirconium ions formed by these vacancies, tend to diffuse into the oxide layer. Oxygen ions are formed at the oxide-gas interface and in turn, diffuse into the oxide layers and the base metal. Because of this, the heat of reaction is thought to be liberated over the entire oxide region, although not necessarily uniformly.

2.1.3 Reaction Rates

Instead of correlating the amounts of each oxide and solid solution formed during the metal-water reaction process, many investigators simply obtain the rate of oxygen uptake of zirconium from the rate of sample weight gain or from the rate of hydrogen formation. The oxygen uptake rate has been determined by several people, with the more recent determinations being those of Baker and Just⁴¹ and White.¹⁷ It is generally agreed among the various investigators and the people in the industry that the following parabolic relation derived by Baker and Just⁴¹ adequately describes these rates:

$$w^2 = 33.3 \times 10^6 t \exp \left(\frac{-45,500}{RT} \right),$$

where w is weight (mg) of zirconium reacted per unit (cm^2) of surface area, t is time (sec), R is the gas constant ($1.987 \text{ cal/mole} \cdot ^\circ\text{K}$), and T is temperature ($^\circ\text{K}$). White,¹⁷ in a recent investigation, suggested the following modification:

$$w^2 = 5.77 \times 10^6 t \exp \left(\frac{-40,500}{RT} \right).$$

However, as shown in Fig. 2.3 the differences in the reaction rates predicted by these two relations are not great. Experimental reaction rate data are also shown in Fig. 2.3, and they are in good agreement with the

Fig. 2.3. Comparison of Predicted and Experimental Rate Data for the Zirconium-Steam Reaction.

values predicted by the above correlations. Similar plots have been prepared by Morrison and his associates^{105,117} and by White¹⁷ that indicated the same conclusion. Also work by Wilson and Barnes²⁰ and by Hesson¹¹⁰ with simulated fuel rods in furnaces gave further support to Baker and Just's relation.

In these relations and in the plot shown in Fig. 2.3, the parabolic rate constants are given in terms of the amount of the reacted metal. It was tacitly assumed that all the reacted metal had been converted into the stoichiometric oxide ZrO_2 , which is not actually the case for the reasons discussed above. White¹⁷ did correlate his results in terms of oxygen added to the metal rather than the amount of metal reacted. However, it is felt that the error introduced by using the correlations in the form shown above in accident analyses is small compared with the other assumptions that are necessary in defining the accident.

It can be seen readily from Fig. 2.3 that the zirconium-steam reaction becomes significant only when the metal temperature is greater than 1000°C . The effects of pressure or any alloying agents such as those found in Zircaloy-2 and Zircaloy-4 on these reaction rates were found to be negligible.

Baker and Just⁴¹ derived their reaction rate relation by using the data obtained in condenser discharge experiments¹¹⁹ and the data obtained by Bostrum¹²⁰ and Lemmon.²⁸ Since they knew the size and initial temperature of the metal particle and the temperature of the water in the condenser discharge experiments, they could predict the rate and the extent of the metal-water reaction. For their mathematical model they assumed that the initial phase of the reaction is controlled by the diffusion of the steam through the hydrogen-rich film surrounding the hot particle and that the latter phase is controlled by the uptake of the oxygen in the solid phase, as described by their parabolic rate relation. At each instant during the time that the reaction was taking place, the reaction rates were calculated by using both mechanisms, and then it was assumed that the actual rate was the smallest of the two.

A comparison shown in Figs. 2.4 and 2.5 of the predicted extent of the reactions and the experimental results for the metal particles indicates good agreement. The dependency of these reactions on the particle diameter, the initial metal temperature, and the water temperature is noted. The increase in the extent of the reaction at the higher metal temperatures and also at the higher water temperatures is due to

Fig. 2.4. Comparison of Computed and Experimental Results of Zirconium Reactions in Room-Temperature Water. (From Refs. 8 and 41)

Fig. 2.5. Comparison of Computed and Experimental Results of Zirconium Reactions in Heated Water. (From Ref. 8)

the greater diffusion rates of the water vapor to the metal surface at these temperatures during the initial part of the reaction. Further support of this diffusion theory is given by the work of Furman,¹²¹ in which the reaction rates of the metal with minute quantities of water in a helium stream flowing by it could be explained by this mechanism. The amounts of the reactions for initial metal temperatures greater than 2600°C are large and are believed to be due to the breaking up of the oxide film into small particles. Explosive reaction rates found at temperatures higher than these are believed to be due to the hydrogen evolution from the particle, which propelled the particles through the water at relatively high velocities. This reduces the resistance of the diffusion of the steam through the hydrogen film to the metal particle and increases the rate of reaction.^{8, 41} Increases in the extent of reaction for the smaller particles are, of course, due to the greater surface area available for the reaction. This is illustrated dramatically in Fig. 2.6.

2.1.4 Zirconium-Air Reaction

Studies have also been made of the oxidation and the ignition of zirconium in air at temperatures greater than 900°C. Analysis of this

Fig. 2.6. Extent of Reaction as a Function of Particle Diameter for Molten Zirconium Spheres Formed in Water. (From Refs. 8 and 41)

reaction is complicated by the fact that the zirconium reacts with both the oxygen and the nitrogen in the air.^{122,123} Nelson¹²² reported the formation of nitrides and oxynitrides in his studies of the oxidation of small (49- to 525- μ -diam) zirconium droplets in air at high temperatures (2340 to 2540°C). White²⁶ recently oxidized some Zircaloy samples in air, and his results are given in Fig. 2.7. The rate of

Fig. 2.7. Weight Gain of Zirconium Alloys by Steam and Air. (From Ref. 26)

oxidation of these samples followed the parabolic law the same as it did for those oxidized by steam. White had reported his results as if all the weight gain was due to the formation of ZrO_2 , which of course gave higher results because of the reaction with the nitrogen in the air. The kinetics of the reaction of zirconium in oxygen atmospheres have been studied by Pemsler,^{38-40,124} and he has found that the reaction rates at higher temperatures (1100 to 1300°C) can also be correlated by the parabolic relation shown in Fig. 2.7. Between 750 and 975°C these rates did not follow any simple law, but at lower temperatures (550 to 650°C), the rates were again parabolic.

Prior to the period when the zirconium-air reaction rate follows the parabolic rule, it is limited by the diffusion of the oxygen and the nitrogen to the metal surface. One study^{125,126} indicated this phase of the reaction to be limited by the diffusion of the oxygen through the nitrogen-rich layer surrounding the metal. The experimental data showed the same variations as predicted by the analytical model, although exact agreement was not obtained because of neglect of the zirconium-nitrogen reaction. This dependency on mass transfer implies that the initial phase of the zirconium-air reaction is dependent on the temperature characteristics of the metal and of the surrounding air. These are, in turn, dependent on the various parameters that influence the heat transfer, such as the size and the shape of the metal particles. In his studies of the oxidation of small zirconium droplets in air, in which he used flash heating techniques, Nelson^{122,127} also observed that the rate of mass transfer of oxygen either through the film surrounding the droplet or within the molten droplet limited the reaction rate. In some cases, Nelson found that the droplets exploded, but he believes that this was due to the nitrogen impurities in the zirconium or in the surrounding air. This explosion phenomenon decreased with increased particle size, and it was not observed for the larger particles.

2.1.5 Reactions of Zircaloy-Clad UO_2 Fuel-Pin Specimens Under Loss-of-Coolant Accident Conditions

Since rates of oxidation of zirconium and its alloys in steam or air environments are, in general, well-enough understood for engineering

purposes, the remaining problem in the reactor accident analyses is to determine the temperature and geometrical characteristics of zirconium cladding and UO_2 fuel, as well as the characteristics of the surrounding steam or air, during the reactor accident conditions. These factors and their interactions are very complex, difficult to define, and hard to simulate experimentally. However, much effort has been directed toward this end for both the loss-of-coolant and the nuclear-excursion accidents.

During the normal operation of a reactor, the temperature distribution inside the fuel pin is a normal parabolic shape, with the temperature at the center of the UO_2 being much higher than that at the edge of this material. There is a significant temperature drop across the boundary or the gas gap between the fuel and the cladding, and the temperature of the cladding approaches that of the primary coolant. In the case of a loss-of-coolant accident, both the heat generation and the cooling rates decrease, and the temperature distributions in the fuel pins tend to become flat. As will be seen in the next chapter, the analytical definition of the temperature distribution history in the fuel pin during this accident is difficult.

Furnace Experiments for Simulating Fuel-Pin Behavior. One of the first attempts to simulate fuel-pin behavior during a loss-of-coolant accident was the furnace experiments of Wilson and Barnes.^{20,61,128,129} In their apparatus, shown in Fig. 2.8, a fuel-pin specimen is slowly elevated into the furnace with steam flowing through it, and the amount of metal-water reaction is measured by the rate of hydrogen evolution. In the first experiment, in which the steam flow was limited and the pin was at 1500°C for relatively long periods of time, the Zircaloy cladding was converted smoothly to the oxide.¹²⁹ This oxide, which was very stable, formed a crucible-like material for the fuel inside it. Subsequent experiments reported for a single fuel pin and for a four-pin cluster exposed to unlimited amounts of steam for about 10 min indicated similar results, although the extent of the oxidation was not so great as for the initial specimen.^{20,61} The temperatures of these latter specimens were 1600 and 1700°C , respectively, with the 1700°C temperature

Fig. 2.8. High-Pressure Furnace for Studies of Metal-Steam Reactions. (From Ref. 128)

being about 200°C above the furnace temperature because of the heat produced from the metal-steam reaction. In all these experiments, there was no sharp line of demarcation between the unreacted metal and the oxide along the length of the pin. When these specimens were cooled, the oxidized cladding tended to break apart, possibly because of the stresses set up due to a phase change of the oxide. An alternate explanation for this breaking apart is the brittleness of the remaining Zircaloy with dissolved oxygen in it. Recent experiments with limited steam flow rates for short periods of time indicated that the maximum amount of metal-steam reaction could be at a location below the midplane (hottest point) of a reactor core.¹³⁰ There were no signs of failure of the specimens used in these particular tests.

Although much information was obtained from these furnace experiments, there are still many uncertainties and unknowns regarding the fuel-pin behavior during a loss-of-coolant accident. It is known that internal pressures inside power reactor fuel pins will increase to high values due to production of fission-product gases, and, as shown in Fig. 2.9, the high-temperature tensile strength of Zircaloy is very low, so these fuel pins might rupture in a loss-of-coolant accident. Also because of their low strength, fuel rods could possibly bow or sag. No studies of these phenomena were made in the furnace experiments. A big difficulty with the furnace experiments is the temperature limitation, which is about 1600°C. As can be seen from the zirconium-oxygen phase diagram, Fig. 2.10, zirconium with oxide on its surface melts at temperatures of 1852°C or higher. (More recent versions of the diagram

Fig. 2.9. Ultimate Tensile Strength of 0.076-cm-Thick Zircaloy-4 Sheet in Argon. (From Ref. 47)

Fig. 2.10. Zirconium-Oxygen System. (From Ref. 29)

of Fig. 2.10 are given by Elliott²⁹ and by Douglass.¹³¹) Therefore no information was obtained regarding the meltdown behavior of the fuel pins under the conditions prevailing in a loss-of-coolant accident without operation of emergency core-cooling systems. Also, no experiments were run in the furnace in which heated fuel-pin specimens were subjected to spraying or flooding of water simulating the action of an emergency core-cooling system.

Rupture Mechanism of Fuel-Pin Cladding. In an attempt to get some understanding of the effects of high internal pressures and temperatures on the rupture mechanism of the fuel-pin cladding, White²⁶ heated some Zircaloy tubes in a furnace with an argon atmosphere. He found for these conditions that the fuel pins would swell and rupture longitudinally at hoop stresses corresponding to the ultimate tensile strengths shown in Fig. 2.9. Subsequent experiments in which Zircaloy tubes were heated in a steam atmosphere gave some very erratic results. The tubes did not swell as much in the steam atmosphere as they did in the argon atmosphere, and the nature of the fracture was more brittle in the steam atmosphere. Work in this area is continuing, and it includes the use of metal that has been in the Dresden I reactor to investigate the effects of radiation.¹³²

Similar rod-swelling and rupture tests are being carried out by General Electric⁴⁴ and Westinghouse.^{45,133} Results of tests by General Electric with Zircaloy-2 tubing from a production lot for the Tarapur reactor agree with those of White. They found that tubing pressurized from 50 to 700 psig with argon and placed in an induction heater swelled and ruptured locally at hoop stresses corresponding to the ultimate tensile stresses shown in Fig. 2.9. Tests with Zircaloy tubing pre-oxidized in air, like the tests by White, showed more brittle failure, with minimal cladding bulging around the point of failure. In this case, the failure was more of a longitudinal crack than a burst through the cladding. Tests by Westinghouse with Zircaloy tubing and free-gas volume and pressure corresponding to those anticipated in a fuel pin also indicated that the rupture is small and local. They found that the tube rupture is in the form of a small longitudinal split about 1/2 in. in maximum length and 1/32 to 3/16 in. wide. These results agree with

those of General Electric and indicate that there will not be gross movement of the UO_2 fuel within the core because of this swelling and rupturing. However, the swelling of the cladding raises the question of the interference with the action of the emergency core-cooling systems, as well as the steam available for the metal-water reaction. Both General Electric and Westinghouse are continuing these studies.^{133,134}

Meltdown Behavior of Fuel Pins. The possible meltdown behavior of fuel pins and the whole reactor core in a loss-of-coolant accident situation with no emergency core cooling is subject to much speculation because of the lack of experimental data.¹ Obviously Zircaloy cladding will melt somewhere between 1850°C , the melting point of the metal, and 2700°C , the melting point of the oxide. In an inert atmosphere, molten Zircaloy appears to have a low viscosity, and it probably would run down the sides of the fuel pin. As the temperature of this molten metal increased, it would tend to dissolve any zirconium oxide present on the surface of the cladding. However, in a steam atmosphere, the metal would continue to react with the steam and form a viscous mass having a higher melting point.^{42,46} If the conditions were such that all the cladding oxidized, it would not melt until it was close to the melting point of ZrO_2 . There is very little eutectic depression of the oxide melting point by UO_2 , as shown in Fig. 2.11.

Because of the uncertainties of cladding behavior under these conditions, the exact fate of the UO_2 fuel is not known. It can be hypothesized that it would eventually melt and form a slag-like mass. This could first occur at the core center line between the midplane and the bottom of the core. The volume of this molten mass of material would then gradually increase in all directions until some of it would start to melt through the fuel grid and fall to the bottom of the pressure vessel.

Induction heating of Zircaloy-clad UO_2 fuel-pin specimens in steam environments is one method being used to get some idea of the behavior of the fuel pins near and at their melting temperatures.^{9,17,57} One of the basic problems in these types of experiment is that the UO_2 couples directly to the induction field at higher temperatures and

Fig. 2.11. UO₂-ZrO₂ Phase Diagram. (From Ref. 135)

therefore does not exactly simulate the accident condition of about equal temperatures for both the UO₂ and the cladding.⁵⁷ If this limitation is recognized and it is considered that the experiments were limited to single or a small number of rod specimens, much meaningful information has been obtained.

Wilson and his associates^{42,46} heated fuel-pin specimens up to 2140°C in a steam atmosphere to simulate the anticipated LOFT loss-of-coolant accident conditions. Local melting of the Zircaloy and the UO_2 was observed, and there was some evidence of an interaction between the molten Zircaloy and the UO_2 . However, there was no evidence of the molten Zircaloy running down the side of or dripping away from the fuel pin. White⁵⁶ also noticed an interaction between the Zircaloy cladding and the UO_2 in samples heated to 1600 and 1750°C. In one case, as shown in Fig. 2.12, there was a band of UO_2 between two layers of solid solutions of ZrO_2 and UO_2 . This will be discussed more in the section on the associated reactions.

Some other interesting experiments were performed by White^{17,47} in which Zircaloy-clad fuel-pin samples were allowed to react with steam to form a uniform layer of oxide on the cladding surface. These samples were then cooled, put into an electric furnace having an inert atmosphere, and subsequently heated to temperatures between 1850 and 2010°C. Results of two of these experiments are shown in Figs. 2.13 and 2.14. These tests indicate that the fuel pins start to fail at the melting point of the cladding material, but the presence of the oxide tends to retain the molten material. However, as the temperature of the pin is increased, the molten zirconium is inclined to dissolve this oxide and wash the UO_2 pellets. Inspection of the zirconium-oxygen phase diagram shown in Fig. 2.10 indicates that this oxide will dissolve in the molten zirconium at the temperatures of these experiments. Epstein mentioned that General Electric has also run several experiments in environments with limited steam in which the molten zirconium had dissolved the oxide during the melting process.¹³⁶ Both Epstein and White indicated that the viscosity of the melted zirconium or Zircaloy in their tests was relatively low.

Effect of Cooling Sprays on Hot Fuel Pins. In none of the experiments described above were the effects of spraying or flooding the zirconium-clad fuel-pin specimens determined. Some experiments for investigating the effects of a water spray on a hot fuel pin were performed recently by Wilson.⁴² In these tests, Zircaloy-clad UO_2 fuel-pin

Maximum temperature 1600°C (Neg. 7053, 75X)

Maximum temperature 1750°C (Neg. 7058, 50X)

Fig. 2.12. Zircaloy-4-Clad UO_2 Heated in 1 atm of Steam at $0.3^\circ\text{C}/\text{sec}$.
(From Ref. 56) (Originals reduced 13.5%)

(A) None

(C) 40 μ

(E) 80 μ

(G) 200 μ

(I) 320 μ

(B) None

(D) 40 μ

(F) 80 μ

(H) 200 μ

(J) 320 μ

Fig. 2.13. Results of Heating Zircaloy-4-Clad UO_2 to 1900°C in an Inert Atmosphere After Various Stages of Oxidation. Numbers adjacent to the samples indicate oxide film thickness. (From Ref. 17)

Fig. 2.14. Results of Heating Zircaloy-4-Clad UC_2 to 2050°C in an Inert Atmosphere After Various Stages of Oxidation. Numbers adjacent to the samples indicate oxide film thickness. (From Ref. 17)

specimens were heated to high temperatures in steam environments in an induction furnace. In each run, a water spray was turned on and the pin temperature was reduced to ambient conditions. In the first experiment, the fuel rod was heated to 2045°C and then cooled from 2045 to 1380°C in 30 sec by the water spray. The pin remained intact during this process, but crumbled after the test. Two additional tests were then run; in the first, the pin was heated to 1750°C and then spray cooled to 110°C in 185 sec, and in the second the pin was heated to approximately 2820°C and then spray cooled to 95°C in 180 sec. Neither pin broke during the experiment, but they did break when the test cell was dismantled. The degree of fragmentation of test pins appears to depend on both the temperature-time history of the pin and the amount of cladding oxidation. These two factors, of course, are not independent. In none of these experiments were any steam explosions observed. Because of this fragmentation, it is difficult to interpret quantitatively the criterion that the cladding metal-water reaction is to be limited to negligible amounts. More work is necessary to determine the effect of emergency core-cooling systems on hot fuel pins including the effects of metal-water reaction on possible fragmentation of fuel pins. This subject should be understood sufficiently to insure that the reactor core does not collapse to a point where decay heat cannot be removed by the emergency core-cooling system. Because of its importance, this additional work should be undertaken at once.

Effect of Dropping Molten Metal into Water. The effect of dropping masses of molten or partially molten metal in limited quantities of water is not well understood. This could happen in a loss-of-coolant accident, with the simultaneous failure of the emergency core-cooling system, in which the melted core would drop into the water remaining in the bottom of the pressure vessel. There has been some experience with this in other industries, such as the steel and aluminum industries,⁶² who indicate the possibility of steam explosions if the molten metal encapsulates some of the water.

Attempts to simulate this situation for a melting reactor core located over a pool of water were made in the flat-top transient

experiments* in TREAT.^{48,137} In these tests, Zircaloy-clad UO_2 fuel pins were suspended over a pool of water at room or higher temperatures and then subjected to a flat-top transient to approximate crudely the loss-of-coolant accident conditions. The specific results to be obtained from these experiments were (1) extent of the metal-water reaction, (2) pressures and temperatures, and (3) final particle size distribution of the fragmented fuel. Three experiments have been run so far, and they are summarized in Table 2.1. Heating times were progressively longer, with the last one being about 50 sec, which is close to the time for the initial fuel-pin melting to take place in a power reactor core. In the last experiment, the pressure in the autoclave kept increasing for about 130 sec, which indicates that part of the pressure transient was due to the nuclear heating and part of it was due to the generation of steam resulting from the cooling of the molten material in the water.

No sudden increases in the autoclave pressure were observed in the flat-top transient experiments, which gives some indication that the meltdown of the fuel pin is a relatively slow and continuous process. Complete destruction of the fuel pins occurred in all these experiments, and the residues from all indicated that molten UO_2 had run out of the pins and left hollow cylindrical segments of cladding. The amount of these cylindrical segments formed was largest in the experiment with the shortest transient and smallest in the experiment with the longest transient. This, of course, indicates the effects of the lower fission heating rates and the more time allowed for the transfer of heat between the UO_2 and the Zircaloy in the experiments with the slower transients. There were many indications that the metal-water reaction took place before and after the fuel pins had collapsed into the pool of water.

Fission heating of the fuel continued after it had fallen into the water, and partly for this reason the metal-water reaction continued

*The fission heating of the sample in the flat-top transient is relatively constant over the heating time, which varies from 12 to 50 sec. This is in contrast to the pulsed transient to which the TREAT fuel-pin specimens are usually subjected. In the pulsed transient, the fission heating of the fuel-pin specimens follows a Gaussian-shaped power-time curve with heating times of about 1 sec or less.

Table 2.1. Summary of Results of Loss-of-Coolant Experiments in TREAT with Zircaloy-2-Clad UO_2 -Core Fuel Clusters^{a,b}

	Experiment Number		
	CEN-217S	CEN-220S	CEN-223S
Transient			
Location of fuel cluster	Above 30°C H ₂ O	Above 100°C H ₂ O	Above 100°C H ₂ O
Duration of flat-top transient, sec	12	32	50
Average heat-generation rate in UO_2 , ^c kw/ft	40	20	11
Average reactor power level, ^c Mw	40	20	11
Fission-energy input, cal/g UO_2	560	770	630
Results			
Metal-water reaction, %	40	44	32
Peak pressure rise, psig	87	750	220
Maximum rate of pressure rise, psig/sec	45	76	2
Final appearance of UO_2 fuel	Complete destruction; fragments and particles; about one-half of cluster dropped into water	Complete destruction; fragments and particles; whole cluster dropped into water	Complete destruction; fragments and particles; whole cluster dropped into water
Average particle size of residue (d_{sv}), ^d mils	91	83	

^aFrom Ref. 48.

^bTen sintered pellets of UO_2 (10% enriched in ^{235}U) per rod. Overall rod dimensions: 5.62 in. long by 0.42 in. in diameter, 25-mil-thick cladding, 3-mil gap between core and cladding, and helium bonded. Three rods with a weight of 254 g of UO_2 and 82 g of Zircaloy-2 per cluster; 750 g of water in autoclave.

^cThe identical values of heat-generation rate and reactor power level are coincidental.

^dThe average particle size of the residue is $d_{sv} = \frac{1}{\sum \frac{w_i}{d_i}}$, where w_i is the fraction by weight

of particles with diameter d_i , as determined by sieve screen analysis.

during this portion of the experiment. Although the mechanisms of heat transfer and fluid flow in these experiments are quite complex, the fact that the extent of the metal-water reaction was only between 32 and 44% is still quite significant. Thermal analysis of the results of these tests also indicated that 20 to 26% of the energy release was due to the chemical reactions. The other significant point of these experiments is that no steam explosions occurred in the autoclave when the molten material dropped into the water. Baker indicated that the transient in these experiments could be extended to 5-min duration to simulate closer the loss-of-coolant accident.²¹ Such an experiment would be difficult to do, however, since the TREAT power level would have to follow the simulated decay heat curve.

Areas for Further Investigation. Work on the meltdown mechanism of the fuel pins and the physical and chemical reactions between water and the melted material should continue. Experiments such as spraying or pouring water on large masses of molten metal should be conducted. (It will be seen later that some work on this subject has been done with aluminum, silver, and uranium oxide.) The purpose of this additional work is determining the technical feasibility of methods other than the emergency core-cooling systems for protection against the loss-of-coolant accident.

2.1.6 Reactions of Zircaloy-Clad UO₂ Fuel-Pin Specimens During Nuclear-Excursion Accident Conditions

The exact thermal-hydraulic history during a nuclear-excursion accident is difficult to predict. In this type of accident, heat is generated at a very rapid rate in UO₂ fuel, which has low thermal diffusivity. This heat is then transferred to the cladding and out to the cooling water. A metal-water reaction could take place if the temperature of the cladding became sufficiently high, and the reaction could provide an additional energy source during the excursion. If the magnitude of the nuclear-energy burst were large, melting, fragmentation, or even vaporization of part of the core would take place. The resulting high temperatures and large surface areas would be favorable for metal-water reaction and rapid transfer of heat to the water. In extreme

cases, this heat could be converted into mechanical energy (steam explosions and/or water hammers) that possibly could rupture the primary coolant system or the pressure vessel. However, it will be seen later that in predicting the consequences of this type of accident, the metal-water reaction does not play a dominant role.

Most of the in-pile experiments relating to the metal-water reaction in nuclear-excursion accidents are those that have been done in TREAT. Early experiments with small fuel pins submerged in water showed a general relation between the extent of the metal-water reaction and the energy input to the UO_2 (Refs. 49-52). These results, shown in Fig. 2.15, indicate that the metal-water reaction does not become significant until the melting temperature of UO_2 is reached, which corresponds to a fission energy input to the fuel of 220 cal/g UO_2 . In some of these experiments, the core material in the fuel pin was pure UO_2 and in

Fig. 2.15. Results of Meltdown Experiments in TREAT on Zircaloy-2-Clad UO_2 -Core Simulated Fuel Elements Submerged in Water. Water at 30°C and 20 psia, except as noted. (From Ref. 52)

others it was a mixture containing mostly ZrO_2 . The difference in these fuels had no bearing on the extent of the metal-water reactions when correlated against the peak adiabatic fuel temperature.⁵⁰

Later scaleup experiments with nine-pin clusters of fuel indicated about the same results for the extent of the metal-water reaction.⁵¹ However, as shown in Fig. 2.16, the sizes of the fragmented particles are larger for the nine-pin clusters. This may be due to the coagulation of the molten particles after they have been formed. Further evidence that this may be happening was observed in the experiments of Parker, Lorenz, and Wilhelm,^{138,139} in which the metal-to-water ratio was greater than in the experiments run by Liimatainen and his associates.⁵¹ Their results for the extent of the metal-water reaction agreed with those given in Fig. 2.15, but they found that the sizes of the fragments remaining at the end of their experiments were larger.¹³⁹ In some of the early TREAT experiments by Liimatainen and others,⁴⁹ the

Fig. 2.16. Degree of Fragmentation of UO_2 -Core Fuel Pins Subjected to a Reactor Pulse. Fuel pins submerged in water. (From Ref. 51)

sizes of the fragments in the residue were measured, and the amount of the metal-water reaction in the excursion experiments was predicted from the data of the condenser-discharge experiments. The agreement of these predicted results with the measured results was found to be quite good. One reason for the good agreement is possibly that the particles of the metal cladding had a chance to react with surrounding water and to cool down to relatively low temperatures before they had a chance to coagulate. In none of the experiments described above was an attempt made to study the heat transfer mechanism in detail. However, it is believed that water boils off from the side of the fuel pin and condenses on the sides of the autoclave used for the experiment.

Recent studies in TREAT were directed to experiments with vibration-packed fuel pins.⁵² The extents of the metal-water reaction in these experiments were about the same as for pins with UO_2 pellets, as shown in Fig. 2.15, but, as shown in Fig. 2.17, the peak pressure rise in the autoclave was found to be substantially higher for the vibration-packed fuel than for the pelletized fuel. This is an indication of the importance of the heat transfer and hydraulic characteristics during a reactor excursion. These characteristics must be studied in detail in order to gain confidence in our understanding of what happens during a nuclear-excursion accident.

In order to help to understand the mechanism of heat transfer and metal-water reaction during a nuclear transient, photographic techniques were used recently.⁵³ Fuel-pin specimens submerged in water contained in a transparent capsule were subjected to nuclear transients and photographed at the same time with a high-speed movie camera. Thermocouples were attached to the surface of the cladding to measure its temperatures. The results of the experiment with the Zircaloy-clad fuel pin are summarized in Table 2.2, where it can be seen that this pin was subjected to three nuclear bursts, each having successively higher energies. No significant melting or metal-water reaction occurred until the final transient, during which the adiabatic temperature of the UO_2 reached 400°C above the UO_2 melting point. However, there was evidence of two pinholes appearing in the cladding during the second transient. The

Table 2.2. Summary of Results of Photographic Meltdown Experiment in TREAT with Zircaloy-2-Clad UO_2 -Core Fuel Rod Submerged in Water^a

Experiment No.: CEN-222T

Fuel rod-dimensions: 5 5/8 in. long by 0.42 in. in diameter

Rod materials: 83 g (10 pellets) of sintered (92% theoretical density) UO_2 , 10% enriched; 27 g of Zircaloy-2 (2.5-mil) cladding; and 600 g of H_2O coolant, initially at 30°C

	Transient No.		
	I	II	III
Transient conditions			
Fission-energy input, ^b cal/g UO_2	165	305	347
Period, msec	238	115	101
Adiabatic UO_2 temperature, °C	2200 (solid)	2850 (melted)	3200 (melted)
Results			
Peak cladding temperature, °C	1155	1700	1800
Metal-water reaction, %	0	0	7
Final fuel rod appearance	Intact	Intact, but photograph indicated local cladding failure	Limited fragmentation, but rod shape retained; partial fuel meltdown and cladding distortion

^aFrom Ref. 53.

^bApproximately 220 cal/g UO_2 is required to heat UO_2 from 25°C to the melting point of 2300°C adiabatically. An additional 60 cal/g is required to melt the UO_2 completely.

Fig. 2.17. Peak Pressure Rise in TREAT Metal-Water Scaleup Experiments as a Function of the Total Energy (Chemical plus Nuclear) per Gram of Water in the Autoclave. (From Ref. 52)

attached thermocouples indicated that the cladding temperature was always much below the fuel temperature during the nuclear excursion.

During the last transient, there was "crinkling," or the inward deformation of the cladding. When the fission-energy input reached 231 cal/g UO₂ (UO₂ had begun to melt), incandescent molten fuel began to penetrate the Zircaloy cladding. When the input reached 280 cal/g UO₂ (UO₂ molten), highly incandescent molten fuel started to penetrate the cladding. However, the cladding retained its general form, and large gas bubbles due to the film boiling were seen. As the fission-energy input increased further, the cladding became incandescent, although it had many dark spots that indicated temperature variations of several hundred degrees around its surface. Convection currents

were established after the nuclear burst that terminated the film boiling and cooled the specimen in about 30 sec. Examination of the pin after the experiment indicated that about 10% of the fuel had passed out of the cladding.

In TREAT experiments, the reactor period cannot be made much lower than about 40 msec. This is higher than the minimum period for a nuclear excursion postulated for some power reactors, which is in the range 2 to 10 msec.^{140,141} Experiments for reactor periods less than the 40 msec value are limited. Some tests were run in connection with the Kiwi-TNT experiment, where the reactor period was 0.6 msec.^{142,143} Information regarding the metal-water reaction in these tests is quite limited, but the available data do show that the Zircaloy cladding breaks up into much finer particles for the shorter periods. No metal-water reaction data were obtained for the Zircaloy-clad fuel pins, but they were obtained for the uranium alloy pins. They showed more extensive reactions for the same energy input to the fuel than those predicted from the results of the TREAT studies. This is believed to be due to the fragmentation of the fuel pins into smaller particles. Therefore the Kiwi-TNT studies do show the possible importance of the effect of the reactor period on the amount of metal-water reaction of the Zircaloy-clad fuel pins that could take place during a nuclear excursion.

Some nuclear-excursion tests were made in the PULSTAR reactor located in Buffalo, New York,¹⁴⁴ in which Zircaloy-2-clad UO_2 fuel pins were subjected to ten successive power bursts. Each power burst brought the UO_2 to its incipient melting point. The minimum period in these tests was 2.83 msec, the maximum fuel enthalpy was 200 cal/g UO_2 , and the fuel pins were cooled by natural convection. Film boiling occurred in these experiments, but no abnormal pressure rise was observed. The integrity of the fuel pins was maintained, although the cladding diameter had increased from 1 to 6% at some local spots and there was random bowing. There was evidence of a limited metal-water reaction by the appearance of a white oxide film on the cladding surface. At the locations of this oxide, there were both film boiling and metal temperatures in excess of 1000°C.

Additional tests with fuel pins and subassemblies for shorter reactor periods are being planned in the Capsule Driver Core (CDC) and the Power Burst Facility (PBF) programs.^{54,145} These two facilities will permit shorter periods with sufficient energy input to cause destruction of the fuel samples. The CDC has an autoclave for testing fuel-pin specimens up to 2 in. in diameter and 60 in. long, and it can be operated at periods down to 3 to 4 msec. The PBF, which will go into operation later, has an in-pile loop to simulate the environment of a power reactor about the test fuel pin, and it will be able to operate at periods down to 1 msec. The in-pile loop in this reactor will contain facilities for circulating high-temperature and high-pressure water, and it will be able to handle test samples up to 4.5 in. in diameter and 36 in. long. Tests in these reactors will give more insight into (1) what conditions are necessary for a fuel rod to fail, (2) what is the mode of the rod failure, and (3) what are the consequences of the rod failure? The metal-water reaction will be investigated in these tests, but the nature and the analysis of the results from these tests will not be limited to this alone. The thermal-hydraulic history and the conversion of thermal energy into mechanical energy will be studied thoroughly.

While much work has been done to determine the behavior of a fuel pin during a nuclear excursion, more work should be done, particularly for fission-energy inputs greater than required to fragment the fuel. For energy inputs below the amount required to melt any of the fuel, the fuel pin remains intact and there is negligible metal-water reaction. The PULSTAR tests did show some local swelling and bowing of the fuel pins, however. At slightly higher energy inputs, molten fuel begins to penetrate the cladding, although the cladding retains its general form and shape. Higher fission-energy inputs result in the fragmentation of the fuel pins and more metal-water reaction.

In assessing these data, the thermal-hydraulic history of the fuel pins, as well as the mechanism for the conversion of the thermal energy into mechanical energy, needs to be known. It is difficult to separate these factors from the metal-water reaction aspect of these experiments, since they are dependent on each other. However, it should be noted

that the low thermal diffusivity of UO_2 limits the rate of cladding heatup during the excursion. If the fission-energy input is limited to values below those for which the cladding is violated, the rate of transfer of heat to the water is limited. For energy inputs higher than this, the rate of heat transfer to the water, the rate of conversion of this heat to mechanical energy, and the rate of metal-water reaction are not well defined. These rates are important in determining when and where there is sufficient energy to get massive core failure, as well as to violate the integrity of the reactor primary cooling system. Tentatively, it appears that an excursion resulting in a fission-energy input greater than 300 to 400 cal/g UO_2 is required to get a severe pressure pulse in the reactor.^{43, 52}

2.2 Reaction of Stainless Steel with Water

2.2.1 Recent Summaries

Since stainless steel is no longer much in use as cladding for the fuel rods in power reactors and since the heat of reaction of stainless steel with water or steam is not so great as that for the reaction involving zirconium, the interest in this material has been less than that for zirconium. However, the recent review articles by Baker^{8, 9, 60} and by Morrison and his associates^{105, 117} for the zirconium-water reaction also have information on the stainless steel-water reaction. In general, this reaction is quite slow until the temperature of the stainless steel reaches 1100 to 1200°C. When the temperature of the stainless steel is increased further to its melting point (~1400°C), it foams into a mushroom-like material, as shown in Figs. 2.18 and 2.19, which increases the available surface area and the overall reaction rate very rapidly. It appears, for engineering purposes, that the rate of reaction of stainless steel above its melting temperature is limited by the amount of steam that reaches its surface.

2.2.2 Reaction Rates and Physical Chemistry

Reaction rates of stainless steel at temperatures below its melting point have been measured both by Wilson and Barnes^{58, 59} and by

Fig. 2.18. Four-Rod Bundle of Type 304 Stainless Steel-Clad UO_2 -Core Fuel After Exposure to Steam at 1 atm and 1600°C . Unexposed fuel rod also shown for comparison. (From Ref. 61)

Fig. 2.19. Closeup View of a Four-Rod Bundle of the Type 304 Stainless Steel-Clad UO_2 -Core Fuel Rods in Fig. 2.18. (From Ref. 61)

White.^{17,56,57} In the experiments of Wilson and Barnes the rate of the reaction of steam with the stainless steel was measured by determining the rate of the hydrogen evolution from the metal sample. They found that for temperatures of 1100 to 1200°C, the reaction rates are nearly parabolic for the first 10 to 20 min, but they increase slightly after this period. At 1300°C, it was found that the initial reaction rate decreased with increasing sample heatup times. At this temperature, the initial reaction rate is approximately linear, with the rate of hydrogen evolution decreasing from about 3.1 to 1.1 ml (STP)/min·cm² of surface area as the time to heat the sample to temperature is raised from 3 to 9 min. After about 20 min, these hydrogen evolution rates are still linear, but they are 2.5 to 1.2 ml (STP)/min·cm², respectively.

White measured the rates of weight gain of stainless steel in steam for temperatures between 1000 and 1350°C. He found that they are linear for an initial period of 6 to 28 min, and then they are parabolic. Results of these experiments for temperatures up to 1250°C are summarized in Fig. 2.20. The curve for the 1250°C data shown in this figure is in reasonable agreement with the data obtained by Wilson and

Fig. 2.20. Steam Corrosion of Type 304 Stainless Steel. (From Ref. 57)

Barnes at 1300°C when they used a 3-min heatup time.⁵⁹ White cross plotted the rate constants for the parabolic portion of the curves shown in Fig. 2.20 versus the reciprocal of the absolute temperature. White's plot is shown in Fig. 2.21, which is based on the weight gain of the stainless steel samples being entirely due to oxygen uptake. This is a reasonable assumption in view of the agreement between these data and those of Wilson and Barnes. Also for temperatures up to 1350°C, White²⁶ has shown that the formation of volatile compounds, such as the iron hydroxides mentioned by Belton and Richardson,¹⁴⁶ is negligible. White correlated the results shown in Fig. 2.21 by the relation.

$$w^2 = 2.4 \times 10^{12} t \exp \left(\frac{-84,300}{RT} \right),$$

Fig. 2.21. Parabolic Rate Constants for Type 304 Stainless Steel-Steam Reaction Versus Reciprocal Absolute Temperature. (From Ref. 17)

where w is weight (mg) of oxygen uptake per unit (cm^2) of the stainless steel surface area, t is time (sec), R is the gas constant (1.987 cal/mole $\cdot^\circ\text{K}$), and T is temperature ($^\circ\text{K}$). The parabolic rate constants for the reaction of steam with Zircaloy-4 are also plotted in Fig. 2.21 for comparison. It can be seen that for temperatures above 1200°C , the reaction rates for stainless steel with steam are greater than those of Zircaloy with steam. However, it should be emphasized that the curve for stainless steel at temperatures above 1350°C is an extrapolation of the data below this temperature.

Because of the foaming action of stainless steel at its melting temperature, it is difficult to measure the reaction rate of this metal with steam at this and higher temperatures in the usual sense because the surface area is unknown. Wilson and his associates^{14,59} measured the rate of hydrogen evolution from stainless steel samples in a flowing steam atmosphere at 1500 and 1600°C . No definitive rate data were obtained, but they found that the reaction rate is a function of the sample heatup rate, size, and shape. However, the effect of the steam pressure in the range 1 to 12 atm is negligible.

The stoichiometry of this reaction was determined by Wilson and his associates¹⁴ by measuring the rate of hydrogen evolution from the stainless steel samples and by x-ray diffraction techniques. X-ray diffraction studies of the oxide product formed on the stainless steel surface at 1500°C indicated that the major portion of this material is Fe_3O_4 or a spinel-type compound. Since this technique cannot distinguish between various compounds of this type, other spinels such as FeCr_2O_4 , NiFe_2O_4 , and NiCr_2O_4 could have formed. If it is assumed that all the oxidation products are these types of compounds, the amount of hydrogen formed from this reaction would be 0.54 liter (STP) per gram of stainless steel. The amount formed in the experiments was 0.51 liter (STP) per gram of stainless steel, and therefore the agreement is excellent. Also, if all the stainless steel reacts to form the spinel-type compounds, the heat of reaction of molten stainless steel to form a molten oxide mixture is calculated to be 155 cal/g.

The stoichiometry of the stainless steel-steam reaction at temperatures between 1000 and 1200°C was also considered by White.^{17,57} Photomicrographs of samples reacted at 1200°C for 5 min (initial linear rate period) indicate that the oxidation product is primarily Fe₃O₄. For samples that reacted long enough to be in the parabolic rate period, the oxide film is still predominately Fe₃O₄, with Fe₂O₃ on the outer surface. White hypothesized that the oxidation process at these temperatures is similar to that for iron, which is controlled by the diffusion of ferrous ions through a layer of FeO next to the metal, the diffusion of ferrous and ferric ions through the layer of Fe₃O₄, and the diffusion of the oxygen ions through the layer of Fe₂O₃. On the basis of the work of Sosman and Hostetter,¹⁴⁷ he believes that one possible reason for the foaming of the stainless steel is the decomposition of the Fe₂O₃ at the higher temperatures.

If it can be assumed that the uptake of oxygen by stainless steel can be described by the formation of Fe₃O₄, White's relation for the parabolic reaction rate of stainless steel with steam can be modified to be

$$w^2 = 6.28 \times 10^{12} t \exp \left(\frac{-84,300}{RT} \right),$$

where w is weight (mg) of stainless steel reacted per unit (cm²) surface area and the other symbols are those described above.

Some condenser discharge experiments with type 316 stainless steel wires were run at ANL,⁸ and the results of these studies are shown in Fig. 2.22. From these studies, two points are significant. First, the amount of reaction obtained with very small metal particles (260 μ) at very high temperatures (3700°C) in heated water is limited. Second, the temperature of the surrounding water has little influence on the extent of the reaction; this implies that the controlling mechanism for this reaction is in the solid phase.

2.2.3 Reactions of Stainless Steel-Clad UO₂ Fuel-Pin Specimens Under Loss-of-Coolant Accident Conditions

Furnace experiments with stainless steel-clad UO₂ rods, which were at temperatures of 1600 to 1700°C, showed the formation of the

Fig. 2.22. Results of Studies of Type 316 Stainless Steel-Water Reaction by the Condenser Discharge Method. The particle diameters of the residue are given in microns. (From Ref. 8)

froth-like material illustrated in Figs. 2.18 and 2.19 (Refs. 61 and 129) with a sharp line of demarcation between the reacted and the non-reacted zones. All indications are, with the instruments used in this experiment, that this line is where the metal reached its melting temperature (1400°C). Results of a typical test¹⁴ with a single fuel-pin specimen (8 in. long by 0.4 in. OD) are shown in Fig. 2.23. In this test, the specimen was slowly inserted into the furnace for 8 min, held at the elevated-temperature position for 2 min, and then withdrawn rapidly to simulate a loss-of-coolant accident. The maximum temperature reached by the top of the specimen was 1600°C and that reached by the bottom was 900°C . About the top third of the specimen had foamed, and it showed extensive reaction, while the bottom part showed only limited reaction. The amount of hydrogen produced corresponded to 37% of the stainless steel, which is in reasonable agreement with the other observations. The steam flow rate and pressure did not appear to have any effect on the rate or the extent of the metal-steam reaction. Tests with four fuel-pin clusters showed that the hydrogen evolution rates are about four times those measured in the single fuel-pin experiment.

Fig. 2.23. Hydrogen Evolution and Temperature of Top End of Sample During Exposure of Type 304 Stainless Steel-Clad Fuel Element to Steam at 1600°C in a High-Pressure Furnace. (From Ref. 14)

Interaction of the stainless steel oxides with the UO_2 pellets was observed, and this will be discussed further in a later section of this chapter. One of the significant observations was that the foaming of the stainless steel tended to bridge the coolant channels, but it did not seem to affect the steam flow in the experiment. It could be argued that this bridging could have an effect on the availability of steam to the stainless steel surfaces that might limit the metal-water reaction. However, most of the reactors that have stainless steel cores are of the open lattice type, and the crossflow of steam in these cores is possible.

The presence of the oxides on the stainless steel fuel pins tends to retard the meltdown of these pins. Experiments by White^{17, 56} showed that the presence of steam, particularly for the slower heatup rates of the fuel pins, tended to retard the molten metal runoff from these pins. He also found that there is less foaming of the stainless steel at the more rapid heatup rates, 3°C/sec versus 0.3°C/sec. As mentioned above, the stainless steel oxides tend to form eutectic mixtures with the UO_2 that tend to cause the cladding to slump.¹⁴⁸ The meltdown experiment

with a type 347 stainless steel-clad UO_2 fuel pin in a 1000-psia steam atmosphere in TREAT also showed that the stainless steel formed the typical spongy material.¹³⁸ This material also tended to slump away from the unmelted UO_2 pellets. Subsequent experiments at higher energy inputs to the fuel pins melted both the stainless steel and the UO_2 (Ref. 139). Particles of stainless steel and eutectics of iron-chromium-nickel oxides and UO_2 were found in the UO_2 clinker at the bottom of the crucible containing the fuel pin and its sample. All these experiments indicate that the oxides of stainless steel will melt in the range 1450 to 1600°C and form a viscous-like material that will slump away from the UO_2 fuel pellets. There appears to be some carrying away of small amounts of the UO_2 from the fuel pellets because of the eutectic formation. Up to these temperatures, the fuel pins appear to be free standing; probably because of the relatively high strength of high-temperature stainless steel, as shown in Fig. 2.24. Future meltdown experiments with stainless

Fig. 2.24. Ultimate Tensile Strength of Type 304 Stainless Steel Sheet. (From Ref. 26)

steel fuel pins are not planned because of the current interest in zirconium.

2.2.4 Reactions of Stainless Steel-Clad UO_2 Fuel-Pin Specimens During Nuclear-Excursion Accident Conditions

Nuclear-excursion effects on stainless steel-clad fuel pins have been studied in a program run simultaneously with that for the Zircaloy-clad fuel pins.^{8,49-51,53} Studies in TREAT, which are summarized in Fig. 2.25, show that there is not much metal-water reaction for stainless steel until the UO_2 fuel starts to melt. When the UO_2 reaches this condition, it starts to melt the stainless steel cladding, which reacts with the surrounding water. A significant borderline case of this is that shown in Fig. 2.26 for a mixed oxide-fuel stainless steel-clad pin, where an energy input of 395 cal/g of fuel* resulted in some melting of the center of the fuel, but the cladding remained intact.

Like the experiments with the Zircaloy-clad fuel pins, much of the interpretation of the metal-water reaction information from these experiments depends on the thermal-hydraulic history during the nuclear excursion. Photographic studies of stainless steel-clad fuel-pin specimens

*The equivalent energy input for the UO_2 fuel is 190 cal/g fuel.

Fig. 2.25. Results of Meltdown Experiments in TREAT with UO_2 -Core Type 304 Stainless Steel-Clad Fuel Pins Submerged in Water at 30°C H_2O and 20 psia. (From Ref. 51)

Fig. 2.26. Results of Meltdown Experiments in TREAT on Mixed-Oxide-Core Stainless Steel-Clad Fuel Pins Submerged in Water. (From Ref. 8) Energy, 395 cal/g mixed oxides; equivalent UO_2 energy, 190 cal/g UO_2 ; period, 78 msec; peak adiabatic temperature, 2500°C . 10x

subjected to nuclear excursions in water have helped to understand the heat transfer mechanism.⁵³ With the same equipment as that used for the Zircaloy-clad fuel-pin tests, a stainless steel-clad fuel pin was subjected to a power burst having a fission energy input of 290 cal/g UO_2 . Analysis of the released hydrogen indicated that about 2% of the cladding

reacted with the water, but the physical inspection of the cladding showed that as much as 10% of the cladding had reacted. The latter figure is in agreement with the information shown in Fig. 2.25. The maximum temperature indicated by the thermocouple attached to the cladding was 490°C, but the foaming appearance on the surface showed that other portions of the cladding reached 1400°C. High-speed motion pictures showed nucleate boiling, followed by film boiling, with the growth of luminous (hot) patches interspersed among the cooler parts of the cladding surface. These hot patches were at the same location as the foaming on the cladding surface, which indicates nonuniform contact between the fuel and the cladding. After the nuclear burst, there was an irregular variation of the cladding temperature for about 5 to 10 sec, followed by the establishment of convection currents, which cooled the specimen in about 30 sec.

The sizes of the fragments produced by the nuclear excursions are summarized in Fig. 2.16. As for the Zircaloy-clad pins, larger size fragments were formed in the excursion experiments with nine-pin clusters than in the single-pin experiments. This again may be due to the fusing together of the molten-metal droplets generated during the excursions. The fuel pin used in the photographic study did not fragment, in contradiction to the information shown in Fig. 2.16. This indicates that there are uncertainties regarding the nature of the breakup of stainless steel-clad fuel pins during nuclear excursions. In addition to these unknowns, the effect of the internal pressure due to the buildup of the gaseous fission products on the fragmentation is unknown. It should be pointed out that although the extent and the nature of the fragmentation in these experiments varied, the extent of the metal-water reactions in all these tests are in agreement.

Other experiments for investigating the behavior of stainless steel-clad UO_2 fuel pins during nuclear excursions are the Kiwi-TNT tests¹⁴² and the CDC tests.⁵⁵ Information regarding the metal-water reaction in Kiwi-TNT tests is negligible thus far. The information obtained recently in the CDC and PBF program^{54, 55} to investigate the behavior of stainless steel-clad fuel pins is still being studied. Factors such as

the lower period of the CDC as compared with that for TREAT (3 msec compared with 50 msec), lower fuel enrichment of the CDC samples, and smaller geometrical size of the CDC samples will be considered.

Like the situation for the Zircaloy-clad fuel pins, the behavior of the stainless steel cladding is known if the fission-energy input to the fuel is below that where any fuel melting could take place. However, for higher energy inputs, the picture is not so clear, particularly about the fragmentation of the fuel pin and the rate of energy transfer from the fragments to the surrounding water. Much of the present emphasis is and should be on Zircaloy-clad fuel-pin behavior during nuclear power bursts. It is possible that much of the information being obtained from these tests could be applied to the behavior of stainless steel-clad fuel pins.

2.3 Reactions with Aluminum

The reaction of water or steam with aluminum is more complicated than the reactions with zirconium or stainless steel.²¹ This is because the vapor phase of the aluminum participates in the reaction and the alloying materials in aluminum also have a great influence. Reactions of water or steam with zirconium and its alloys and with stainless steel take place in the solid phase and are pretty much independent of the alloy content. Because of the limited interest in aluminum for use in light-water power reactors, this review of the metal-water reaction of this material is limited to experiments relating to aluminum behavior in nuclear excursions. The reason for the interest in these experiments is that the only reactors of concern that have had destructive nuclear excursions are those that have aluminum-uranium alloy plate-type fuel elements.

2.3.1 Reactions of Aluminum-Uranium Alloy Fuel-Plate Specimens During Nuclear-Excursion Accident Conditions

The results of the TREAT experiments shown in Figs. 2.27 and 2.28 have been summarized well by Baker.^{8,60} These results indicate a threshold of energy above which the extent of the metal-water reaction

Fig. 2.27. Aluminum-Uranium Alloy Fuel-Plate Meltdown Experiments in TREAT. (From Ref. 60)

Fig. 2.28. Average Particle Size of Aluminum-Uranium Alloy Fuel Plates After Irradiation in TREAT Versus Nuclear-Energy Input. (From Ref. 8)

increases very rapidly. In room-temperature water with 20-psi helium overpressure, the extent of the reaction at peak temperatures of 1200 to 1400°C is about 15%. Increasing the helium overpressure to 1000 psi increases the extent of the reaction, and heating the surrounding water in addition to this further increases it. Residues from the latter experiments and the experiments with room-temperature water in which the metal temperature exceeded 1400°C all indicate that vapor burning had taken place. One experiment with irradiated SL-1 fuel material indicates that preirradiation has no apparent effect on either the residue or the extent of the metal-water reaction.^{60,149}

As for the TREAT studies of the other fuel specimens, the thermal-hydrodynamic history and the nature of the fragmentation of the specimen are important in interpreting the results for the metal-water reactions. Some recent photographic studies of SPERT 1-D aluminum-uranium fuel specimens in TREAT with a fission-energy input of 751 cal/g indicated that the general sequence of events is as follows:⁶¹

1. the fission power rises,
2. the water boils,
3. the fuel melts into a globule,
4. glowing is observed and a bubble of hydrogen forms,
5. the brightness of the sample increases and ignition occurs,
6. the sample fragments, and
7. the sample burns until it is quenched.

As mentioned in the ANL report,⁶¹ it is particularly interesting that the fragmentation did not take place until after ignition. They explained that the fragmentation apparently results from the water column driving the globule against the bottom of the vessel. Water is forced upward and forms a bubble of steam, and then the collapse of this bubble forces the return of this water to the bottom of the vessel and causes fragmentation of the sample.

2.3.2 Impact of Water on Molten Aluminum

Some particularly interesting results were obtained by Wright⁶³⁻⁶⁵ when he allowed a column of water to impact on a pool of molten aluminum.

He observed the following pressures:

Condition of Aluminum	Temperature of Aluminum (°C)	Pressure (psia)
Solid	600	200
Molten	700	600
	850	2000
	950	2900
	1000	5800

The molten aluminum broke up into irregular particles at the time of the water impact. Although there was hydrogen produced by the aluminum-water chemical reaction in these experiments, it is felt that the contribution of the energy from the reaction to the pressure pulses was negligible. Substituting molten silver, which is chemically nonreactive with water, for molten aluminum in these experiments verified this hypothesis. The tests with silver showed that the high pressures could be explained by the thermal process alone.

Mention should also be made of the work of Long,⁶² who dropped relatively large masses of molten aluminum into water. Violent explosions occurred when there was some triggering mechanism capable of dispersing the molten metal under water. The triggering mechanism in Long's experiments was the expansion of a thin layer of water trapped under the sudden rush of molten metal into steam. No gross metal-water chemical reactions were observed in Long's experiments. Both these experiments do show the possibility of steam explosions when water is sprayed or poured on large masses of molten material such as a melted reactor core. More work should therefore be directed to this subject.

2.4 Reactions with UO₂

Studies of the reaction of UO₂ at elevated temperatures with steam have not been as extensive as the studies of reactions of cladding materials with steam. However, the UO₂ reaction has been studied by Wilson, Barnes, and Baker¹⁵ and by White,^{17,26,47} who indicate that the equilibrium reaction products are those listed below:

Temperature ($^{\circ}\text{C}$)	x in UO_{2+x}
1000	0.27
1200	0.21
1300	0.193
1400	0.183
1500	0.174
1600	0.166

Wilson, Barnes, and Baker determined experimentally that the equilibrium reaction product at 1500°C is $\text{UO}_{2.17}$, which is in agreement with the value stated. As will be seen later, the presence of hydrogen, such as that formed by the cladding-water reaction, tends to retard the UO_2 oxidation. In steam environments, the rate of oxidation of UO_2 initially follows the parabolic law until it tapers off to zero as equilibrium conditions are approached, as shown in Fig. 2.29. White¹⁷

Fig. 2.29. Oxygen-to-Uranium Ratio After Exposure of UO_2 to Steam at 1500°C and 1 atm Pressure. (From Ref. 15)

correlated the reaction rate during this initial period by the parabolic relation

$$w^2 = 1.64 \times 10^5 t \exp \left(\frac{-50,800}{RT} \right),$$

where w is the weight gain (mg O_2) per unit (cm^2) of surface area, t is time (sec), R is the gas constant ($1.987 \text{ cal/mole} \cdot ^\circ\text{K}$), and T is temperature ($^\circ\text{K}$). Further calculations by White²⁶ indicate that this reaction for temperatures above 1000°C can be described by the diffusion of oxygen ions in UO_2 . He also observed that the volume of the UO_2 specimens increased 3 to 6%. The heat generated by this reaction is negligible. Calculations by Wilson, Barnes, and Baker¹⁵ indicate that for temperatures between 850 and 1100°C , this reaction is actually endothermic to the extent of 20 cal/g UO_2 , but this number approaches zero at the higher temperatures.

Calculations by Wilson, Barnes, and Baker¹⁵ showed that in a steam atmosphere containing 10% hydrogen, which could exist around a fuel pin with metal cladding, the value of x in the equilibrium reaction product UO_{2+x} is 0.00 at 1027°C and 0.02 at 1427°C . This indicates that the steam would react with the zirconium or the stainless steel cladding before it would react with the UO_2 , and this was confirmed experimentally by White.¹⁹ Another demonstration of this was the TREAT experiments by Liimatainen and Testa,¹⁵⁰ in which it was found that UO_2 without cladding reacted with water. However, the extent of this reaction in TREAT for metal-clad fuel specimens was negligible.

Mention should be made of the experiments of Wright,⁶⁵ in which he allowed a column of water to impact on hot powdered UO_2 . Tests with UO_2 at initial temperatures of 800 and 1200°C resulted in generated pressures considerably lower than those observed for the impact of water on aluminum at the same temperatures. Wright indicated the need of additional tests with molten UO_2 to determine the possible generation of high pressures when it came into contact with water. Tests of molten UO_2 dropping into water were performed by Gibby,⁶⁶ whose work indicated limited chemical reaction and that the extent of the oxidation of the UO_2 is dependent on the initial water temperature. Attempts to measure

the pressure transients during these experiments were unsuccessful, however. The end product in these experiments was not a powder but, rather, a very friable material that could be easily reduced to a coarse powder. More work should be directed toward this type of testing to determine whether there is a possibility of steam explosions when molten UO_2 drops into a pool of water.

The presence of oxygen or air enhances the oxidation of the UO_2 .^{19,47} The concern for the UO_2 -air reaction is that U_3O_8 will be formed when the UO_2 is in the temperature range 300 to 1500°C (Ref. 151). This compound has a lower density than that of UO_2 , 8.4 g/cc for U_3O_8 compared with 11.0 g/cc for UO_2 , and the lower density causes swelling and the possible collapse of any of the fuel pins that may have ruptured cladding. Much is known about the UO_2 -air reaction, but further work is needed in order to clarify the breakup of the UO_2 fuel rods. Although this may be important, other work should be given priority; that is, how the cladding fails, etc.

2.5 Other Reactions

2.5.1 Types of Reactions

In addition to the reactions discussed above, several other chemical reactions are possible in the various reactor accidents. These reactions are not necessarily exothermic, but they can affect the nature of the core disassembly and collapse. The cladding metal can react with the UO_2 and can form low-melting eutectic mixtures. Other low-melting eutectics can be formed between cladding material and the control rods or the core support structure. The control rod materials themselves could possibly react with the surrounding steam. In addition, hydrogen formed by the metal-water reaction in the lower part of the core could possibly be absorbed in the upper part of the core. All these reactions primarily affect the mode of the core disassembly and are of primary interest when the emergency core-cooling system fails to operate in a loss-of-coolant accident. There is also interest in any possible chemical reaction between refractory materials and

molten reactor core materials. This interest is generated by the often suggested "core catcher" for containing a melted reactor core resulting from the loss-of-coolant accident and the failure of the emergency core-cooling system.¹

2.5.2 Reaction and Eutectic Formation Between Zirconium Cladding and UO₂ Fuel

As noted above and shown in Fig. 2.12, some of the Zircaloy-clad fuel-pin specimens heated in a steam environment showed a uranium-rich zone in the ZrO₂ film.⁵⁶ The mechanism for this is difficult to define, but the formation of the uranium-rich zone appears to be initiated by the reduction of the UO₂ by the zirconium metal adjacent to it. This reduced uranium diffuses into the cladding and is subsequently oxidized again by the oxygen ions diffusing through the ZrO₂ layer. As had been mentioned by White,⁵⁶ this would require a slower diffusion rate for uranium through zirconium than for oxygen through zirconium, which appears to be reasonable. The kinetics of the reduction of UO₂ by zirconium and Zircaloy-2 have been studied by Mallet and his associates,^{67,68} but their studies are limited to temperatures below 1100°C. The reaction rates at the temperatures they used are too low to be of concern here, but their data do indicate that the rates could be somewhat higher at the higher temperatures that could be encountered in the loss-of-coolant accident.

The interest in this reaction is due to the possibility that a low-melting ternary mixture of zirconium, uranium, and oxygen might form between the fuel and the cladding and influence the character of the fuel meltdown. Some work on the ternary phase diagram for these three elements has been done by Saller⁶⁹ but more is required to determine whether such a low-melting eutectic is formed.¹⁵² Before such work is done, however, more effort should be devoted to determining the gross behavior of the fuel pins during the melting process. Parker and Wilhelm²² measured the melting point of a mixture of ZrO₂, Zr, and UO₂ prepared by melting a Zircaloy-clad UO₂ fuel specimen in air by induction heating. They found that the melting point of this mixture was 2150°C in air and 2450°C in a vacuum.

2.5.3 Interaction Between Zirconium and Stainless Steel

The interaction of molten zirconium with the surrounding stainless steel structure in a reactor core is not well understood. Zirconium and its oxides have higher melting points than stainless steel and its oxides, and conceivably they could melt the stainless steel. Also, as shown in the zirconium-iron phase diagram, Fig. 2.30, eutectics having melting points as low as 934°C could be formed. The behavior of the stainless steel structure adjacent to the molten zirconium could depend on the heat transfer characteristics of the two materials. Experiments in air in which molten zirconium ran down the side of a stainless steel specimen indicated no real significant damage to the stainless steel.¹⁵³ However, Parker, Lorenz, and Wilhelm¹³⁹ have observed the melting of stainless steel by a molten mixture of Zr, ZrO_2 , and UO_2 at the bottom of the crucible in their TREAT experiments. Lorenz¹⁵⁴ told of seeing the penetration of zirconium into stainless steel and the formation of eutectics between these two materials, with some having melting temperatures as low as 900°C. There is evidence that if the

Fig. 2.30. Zirconium-Iron System. (From Ref. 70)

oxide film on either the zirconium or the stainless steel remains intact, no interaction between the two materials will take place.¹⁵⁵ These metals will interact, however, if both oxide films are broken.

Definitive experiments for the phase relations between zirconium and its oxides, uranium and its oxides, and stainless steel and its oxides are lacking, partially because of the difficulty of getting to the melting temperatures in the first place. However, engineering experiments to get some knowledge of the behavior of these materials adjacent to stainless steel are required.

2.5.4 Eutectic Formation Between Stainless Steel Oxides and UO_2

As mentioned above, Wilson²³ in his furnace experiments with stainless steel-clad UO_2 fuel pins has seen some eutectic formation between the oxides of the cladding and the fuel. Also, as mentioned above, definitive data on such eutectics are lacking, but some tests for determining the melting point of stainless steel oxide-uranium dioxide mixtures were run by Parker and Wilhelm.²² Data from these experiments (Table 2.3) indicate that eutectics are formed that have melting points in air approaching those of stainless steel and its oxides. This is in agreement with data of a Russian paper²⁴ in which it is reported that a mixture of 50 mole % UO_2 and 50 mole % Fe_2O_3 melted easily at 1370°C . Although more work is needed in this area, effort should still be concentrated on the Zircaloy-clad UO_2 fuel elements and their interactions with the surrounding stainless steel core structure.

2.5.5 Reactions Between Refractory Materials and Molten Reactor Core Materials

As mentioned above, there is interest in refractory materials for use in the often suggested "core catchers" for additional protection in case of a loss-of-coolant accident. The many problems associated with such devices¹ are not considered here; the intent here is only to point out some of the chemical reactions. Very little is really known about the chemical behavior between molten reactor core materials and the refractory materials.¹ There is some Russian data on the melting behavior in air of mixtures of UO_2 and other oxides such as Al_2O_3 and

Table 2.3. Observed Melting Points of UO₂-Stainless Steel Oxide Mixtures^a

Mixture No.	UO ₂ Content of Mixture (wt %)	Melting Point (°C)	
		In Air	In Vacuum
1	76 ^b	1435	1750
2	86 ^c	1475	2250
3	93 ^d	1650	2600

^aFrom Ref. 22.

^bApproximate composition if all the stainless steel cladding in a given reactor core oxidized and mixed homogeneously with all the UO₂.

^cMixture contains one-half the normal amount of stainless steel oxide that would be present in oxidized fuel elements.

^dMixture contains one-fourth the normal amount of stainless steel oxide that would be present in oxidized fuel elements.

ZrO₂ (Ref. 24). Some qualitative experiments were run recently by Row⁷¹ in which molten UO₂ was held in contact with various refractory materials for 20 to 25 min. He found that Al₂O₃, MgO, SiC, and ZrO₂ refractory-grade materials, as well as graphite, showed good resistance to penetration by molten UO₂. (Neither concrete nor sand could withstand the temperatures of these tests.) However, interaction was observed between UO₂ and all these materials, with the exception of graphite. In the case of graphite, it should be remembered that the hot UO₂ could heat the graphite to a temperature at which it would react easily with the surrounding air.

2.5.6 Reactions with the Control Rod Materials

The neutron-absorbing material in the BWR control rods is boron carbide and that in the PWR control rods is a silver-cadmium-indium alloy. Both these materials are normally encased in stainless steel tubes. During an unlikely nuclear reactor accident, it is possible that

this stainless steel could react and expose the neutron-absorbing material.

Boron carbide can react with air at temperatures above 450°C to form a B_2O_3 oxidation product.⁷² However, water vapor reacts with the B_2O_3 product to form a volatile boric acid molecule, and the rate of this reaction is dependent on the vapor pressure of the water in the air. In some cases this latter reaction is more rapid than that for the oxide formation reaction, which maintains a clean boron carbide surface. This was found to occur for temperatures from 250 up to 550 to 600°C for air with dew points ranging from 25 to 70°C. At higher temperatures the rate of the B_2O_3 formation is higher.

For the control rods containing the silver-cadmium-indium alloys, no significant metal-water reaction of the control rod stainless steel sheathing would take place until the temperatures were greater than about 1200°C. Little has been found regarding the metal-water reaction of silver-cadmium-indium alloys at these temperatures, but it appears that the alloy would simply flow out of the control rod, since it has a melting point in the range 775 to 826°C (Ref. 73).

2.5.7 Zirconium-Hydrogen Reaction

The nature of the reaction of the zirconium in the upper part of the core with the hydrogen formed by the metal-water reaction in the lower part of the core during a loss-of-coolant thermal transient is not known with complete certainty. Also the effect of dissolved hydrogen on the physical and mechanical properties of zirconium at these high temperatures is unknown.³² At temperatures below 1050°C, the zirconium-hydrogen phase diagram is understood well enough,^{29-31,33} but these temperatures are below those at which the amount of the metal-water reaction is very great. At temperatures above 1000°C, zirconium hydride decomposes, but hydrogen is still soluble in the zirconium metal. However, it should be noted that higher pressures are required for this absorption of hydrogen to occur.³³ Also the presence of small amounts of water vapor in the gas surrounding the fuel pin or the oxide on the zirconium metal surface greatly reduces the hydrogen

absorption in the metal.¹⁹ Tests by White²⁶ with 1/2-in.-diam spherical Zircaloy samples in atmospheric-pressure steam indicated negligible absorption of hydrogen at 1200 and 1600°C. However, Lemmon²⁸ reported absorption of 4.7 to 12.5% of hydrogen formed by the reaction of 50-psia steam with cylindrical Zircaloy samples 1/2 in. in diameter and 2 in. in length. This discrepancy could be due to the differences in the sample geometry and/or the steam pressure. Attention should be given to this particular reaction, and one suggested method is to use a full-length electrically heated mockup of a power reactor fuel rod with steam flowing by it and to observe any possible reaction or its effects.

2.6 Similarities and Dissimilarities Between the Various Metal-Water Reactions

As may be seen above, the basic nature of the reaction of steam with each of the metals commonly used in reactor cores is quite different. For zirconium and stainless steel, the reaction takes place in the solid phase of the material, but for aluminum the vapor phase of the metal enters into the reaction mechanism. Reaction rates for both zirconium and stainless steel are understood well compared with the other conditions that exist during an unlikely accident, and therefore, from a safety viewpoint, further work on these rates is not required.

The reactions of both zirconium and stainless steel after an initial induction period can be correlated by the parabolic rate relations with the usual Arrhenius rate constants. During the initial induction period, the rate of diffusion of the steam through the surrounding gas film into the reacting metal appears to be the limiting factor. In both these reactions, pressure appears to have little influence. The zirconium-steam reaction is significant only when the metal temperature reaches 1000°C, and it generally can be ignored below this temperature. In situations such as in a loss-of-coolant accident, where the surface areas are well defined, the overall reaction rates of zirconium with steam in the reactor core can be calculated. In the case of stainless steel, the reaction with steam becomes significant when the temperature of the steel is greater than 1200°C. However, when the

temperature of the stainless steel reaches its melting point ($\sim 1400^{\circ}\text{C}$), the steel foams and the surface area is increased greatly. In this case, the reaction rate has to be calculated on the basis of a unit weight of the material. As may be seen in the next chapter, this reaction is usually limited by the amount of the available steam.

2.7 Hydrogen-Air Reaction

As may be seen in Table 1.3 of Chapter 1, one of the most important potential sources of energy release following a metal-water reaction in a reactor core is the reaction of the hydrogen formed by the metal-water reaction with the surrounding air. It is conceivable that this material could react explosively with the air in the containment vessel and cause appreciable damage or even rupture of this vessel. In the course of gathering information for this review, it became very apparent that the quantity of literature relating to the hydrogen-air reaction and its effects is enormous. Because of this and because of the limited time available, this subject was not studied in complete detail. However, sufficient information was obtained to indicate the nature of this reaction and some of the problems associated with it.

One short review paper regarding this reaction and its applicability to reactor safety analysis was written recently by Moore and Gilby.⁸⁰ Some earlier reviews on the same subject are those of Morrison and his associates^{78,105} and of Jensen.¹⁰³ They have all indicated need for better understanding of this reaction. However, as pointed out by Moore and Gilby, there are many more uncertainties associated with the definition of the accident, including the rate of hydrogen production, than there are with the basic reaction rate data.

2.7.1 Flammability and Detonation Limits

The flammability and detonation limits for hydrogen-steam-air mixtures often referenced in the literature and usually used by the reactor manufacturers are those reported by Shapiro and Moffette.⁷⁴ The flammable limits are defined as the points where the hydrogen flame propagates itself. If there is an igniting source present,

hydrogen can partially burn below its flammable limit, but the flame will not propagate itself. Detonation limits are defined as the points at which the shock wave propagating from the burning mixture produces sufficient compression of the gases in the shock front for continuing ignition to occur. The data shown in Fig. 2.31 are based for the most part on the works of Zabetakis^{75,76} and of Coward and Jones.⁷⁷ This diagram gives the range of compositions for detonation, the range where the hydrogen would react rapidly but would not detonate, and the range where the hydrogen would not react at all. It can be seen that the range of compositions for detonation to take place is limited. This gives some indication that detonation of the hydrogen in the containment vessel is not very likely. But this subject has to be studied thoroughly before saying that it would not happen.

Actually Fig. 2.31 is a simplification of a very complicated process. As stated by Morrison and his co-workers,⁷⁸ and by Lewis and Von Elbe,⁷⁹ the reaction of hydrogen with air is made up of a series of

Fig. 2.31. Flammability Limits of Hydrogen-Air-Steam Mixtures.
 (From Refs. 74 and 103)

several reactions. The rates of these reactions are influenced by several variables, such as pressure, temperature, size of the vessel in which the experiment is being performed, and the direction of the burning hydrogen flame (i.e., whether it is up, down, or horizontal). Moore and Gilby⁸⁰ state that attempts to explain these flammability limits theoretically have not met with much success.

Recent reviews and calculations of the detonation limits of hydrogen-air-steam mixtures have been made by Moore and Gilby⁸⁰ and by Mathews.⁸¹ At the higher pressures encountered in shocked gases, it would be expected that the detonation limits would be governed more by thermal effects than by the branched-chain theory (basic chemical reaction rates). However, Belles¹⁵⁶ used the branched-chain theory appropriate to the second explosion limit (defined below in the section on spontaneous ignition temperatures) and found good agreement between theory and experiment for hydrogen-oxygen and hydrogen-air mixtures. Moore and Gilby extended this theory to hydrogen-air-nitrogen mixtures and obtained reasonably good agreement with the experimental results. With the same theory for hydrogen-air-steam mixtures, they calculated that 11% steam was sufficient to completely suppress any detonation. The reason for this is that the H_2O molecule is much more effective than the N_2 molecule in suppressing the active radicals in the hydrogen-air reaction. By the same theory, Mathews⁸¹ also found that steam is very effective in suppressing detonation. Moore and Gilby noted that the effective heat capacity of water vapor is only about 35% greater than that of nitrogen and that it could be argued, without experimental data, that detonation is only a thermal process. For this situation, the detonation limits would be about the same for both the hydrogen-air-steam and hydrogen-air-nitrogen mixtures. Use of these more pessimistic limits has been recommended until more data are obtained. It is interesting to note that the "assumed detonation limit" in Fig. 2.31 is about the same as that calculated by Moore and Gilby for the hydrogen-air-nitrogen mixtures. Mathews also calculated more conservative limits for the hydrogen-air-steam mixtures because of the lack of experimental data. His conservative limits are based on the third explosion limit

theory (defined below in the section on spontaneous ignition temperatures) and that the H_2O molecule was only as effective as the H_2 molecule in suppressing the active radicals in the hydrogen-air reaction. It clearly can be seen that the calculations describing the effectiveness of water vapor of suppressing the detonations are being questioned. More experimental data could resolve this unknown and possibly help in clarifying the uncertainties regarding possible detonation within containment vessels.

2.7.2 Spontaneous Ignition Temperatures

As will be seen in the next chapter, many of the loss-of-coolant accident analyses indicate that the hydrogen is above its spontaneous ignition temperature when it leaves the primary coolant system, while other analyses indicate that it does not. Moore and Gilby⁸⁰ and Mathews⁸¹ have reviewed this subject recently, and they state that there is some experimental information for both static and dynamic systems.

For static systems in which there is a hydrogen-containing gas mixture in a vessel, a theory exists as to the effect of the various parameters, such as the vessel size, for mixtures other than the hydrogen-air-steam mixtures. The experimental data that are quoted most often to agree with this theory are the ignition temperatures given in Fig. 2.32 for a stoichiometric hydrogen-oxygen mixture in a 7.4-cm-diam vessel. This curve shows three limits for the spontaneous ignition temperature, and it is interesting to note that when the pressure is 1 to 2 atm (such as the pressures existing in the containment vessel during a reactor accident), the spontaneous ignition temperature exceeds 550°C. However, these limits are greatly influenced by the presence of an inert gas such as nitrogen, steam, and the vessel diameter. Increasing the vessel diameter reduces these limits. Moore and Gilby calculated that the spontaneous ignition temperatures for a hydrogen-oxygen mixture in a 130-ft-diam vessel at a few atmospheres pressures are lower than those for the same mixture in the 7.4-cm-diam vessel by about 280°C. Mathews calculated the same trend in his work. However, nitrogen increases these temperatures to some extent, and water vapor increases them greatly.

Fig. 2.32. Explosion Limits of a Stoichiometric Hydrogen-Oxygen Mixture in a Spherical KCl-Coated Vessel of 7.4 cm Diameter. First and third limits are partly extrapolated. The first limit is subject to erratic changes. (From Ref. 79)

Measurements of spontaneous ignition temperatures of hydrogen-air-steam mixtures in small vessels having geometries not typical of those of reactor containment vessels also were reported by Shapiro and Moffette.⁷⁴ These results indicate that the addition of 30 vol %

steam to a hydrogen-air mixture increases the spontaneous ignition temperature from 515 to 545°C. They also reported that the effect of the hydrogen-to-air ratio on these limits is quite noticeable. Moore and Gilby⁸⁰ question the conclusions derived from these results because thermal effects that were taking place during these experiments could have had a considerable effect on the data.

Spontaneous ignition temperatures measured for dynamic systems in which a heated mixture of hydrogen and steam flows out of a pipe into atmospheric air have been reported by Shapiro and Moffette.⁷⁴ These temperatures, shown in Figs. 2.33 and 2.34, are between 680 and 835°C. Placing an object in front of this jet of hydrogen-steam mixture reduces the ignition temperature to about 520°C, which is about the same as that observed for the static system.⁷⁴

It can be seen that although much is known about the spontaneous ignition temperatures of hydrogen-air-steam mixtures, there are many uncertainties regarding them for the gas mixtures that may exist in

Fig. 2.33. Variation in the Minimum Spontaneous Ignition Temperature with Exit Velocity of Hydrogen Flowing Through a 0.54-in.-diam by 59-in. Stainless Steel Pipe into Unheated Air at 1 atm Pressure. (From Ref. 74)

Fig. 2.34. Variation in the Minimum Spontaneous Ignition Temperature of Hydrogen-Water Vapor Mixtures Flowing Through a 0.54-in.-diam by 59-in. Stainless Steel Pipe into Unheated Air at 1-atm Pressure. Exit velocity: 1.6 to 71 fps. (From Ref. 74)

large power reactors during accident conditions. Certainly more work is needed for both static systems simulating these mixtures in reactor containment vessels and for dynamic systems for such mixtures passing through a break in the primary coolant system into the reactor vessel. As stated by Moore and Gilby,⁸⁰ the worst case with respect to the hydrogen-air reaction may not be that in which all steam flowing through the reactor core reacts with the cladding but, rather, that in which a limited amount of steam reacts with the cladding. In the latter case,

it can be hypothesized that hydrogen can be formed at a relatively slow rate and it may therefore cool to below its spontaneous ignition temperature prior to its entrance into the containment vessel. It can then be hypothesized further that this hydrogen could pocket and form an explosive mixture within the containment vessel.

2.7.3 Radiolytic Hydrogen

There has been some concern with respect to the potential hazard due to the accumulation of hydrogen over long periods of time from the radiolytic decomposition of water. Like the hydrogen-air reaction, this process is very complicated and is actually made up of a series of reactions. There is considerable information regarding this in the literature, and a good recent summary pertinent to pressurized-water reactors is presented in the work of Jenks on the operating behavior of the HFIR coolant.⁸² For the boiling-water reactors, a good summary of the radiolytic decomposition of the water is presented by Breden.⁸³ Another recent report covering radiolytic gas behavior in both the pressurized- and the boiling-water reactors is that by Jenks and Griess.⁸⁴

2.8 Effect of Metal-Water Reaction on the Nature of the Released Fission Products

The subject of fission-product release from reactor fuel elements under accident conditions is complicated, and much literature has been written on this subject, as can be seen from the work of Browning and Miller and their associates,¹⁵⁷⁻¹⁵⁹ and from the review of Morrison and his co-workers.¹⁰⁵ Details of this are beyond the scope of this paper, but a few general points indicate that metal-water reactions can influence the nature of the fission-product release from these fuel elements. First, they cause higher fuel element temperatures and the formation of eutectics that tend to release greater quantities of the fission products. Second, they create a reducing atmosphere around the fuel pins that influences the chemical nature of the fission products leaving the fuel element. Some of the fission products for which this is noticed are ruthenium, tellurium, cesium, and iodine.

3. APPLICATION OF DATA FOR METAL-WATER AND ASSOCIATED REACTIONS TO REACTOR ACCIDENT SITUATIONS

Methods for predicting the rates and extent of metal-water and other chemical reactions during hypothetical reactor accident situations from the basic data covered in Chapter 2 are considered here. Experiments relating to the development of the methods are discussed, and the division between these experiments and those described in the previous chapter can be seen to be somewhat arbitrary. This comes about because of the many related factors that must be considered in examining a postulated accident. It may be seen that the prediction of the consequences of chemical reactions in such accidents can be evaluated best by using total-system (integral) models. As mentioned before, many of the projects relating to these methods and experiments sponsored by the USAEC are summarized in a draft of a descriptive report prepared by the Water-Reactor Safety Program Office.³

Information on nuclear excursions and loss-of-coolant accidents in reactors that is pertinent to these hypothetical accidents in power reactors is presented. The reactors other than power reactors that are discussed include BORAX-1, SPERT-1, and SL-1, which experienced destructive nuclear excursions, and LOFT, which is being built for studies of intentional loss-of-coolant accidents. Comments are made about the various analytical methods and their results, but they should not be considered as an exhaustive evaluation of these analytical methods, nor should any of this information be construed as judgment of the merits of one reactor compared with another. However, if the information presented in this chapter were omitted, the understanding of chemical reactions in reactor accidents would be incomplete. It will be seen that the uncertainties in defining the accident conditions in a reactor plant greatly exceed the uncertainties in the basic chemical reaction data given in the preceding chapter.

As mentioned in Chapter 1, engineered safety features are incorporated in power reactors to prevent or mitigate consequences of nuclear excursions and loss-of-coolant accidents. It will be seen that these safety features can limit or even prevent metal-water reactions in a

reactor accident. Only when these safety features failed would the chemical reactions be of much concern in the accident situations. It is not the purpose of this review to evaluate the design and reliability of these safety features. Emergency core-cooling systems are frequently mentioned in connection with the loss-of-coolant accident, and they are being reviewed in detail by Lawson² in another review report of this series.

In the unlikely event of partial or complete failure of the engineered safety features in a reactor accident, there would be concern regarding possible chemical reactions and the part that they take in a complex sequence of events that might ultimately lead to containment vessel failure. It is conceivable that vessel failure could be caused by a shock wave or a missile created directly or indirectly by a chemical reaction. The subject of shock waves and missiles is being reviewed by Gwaltney¹⁶⁰ in another report of this series. Another possible method of containment vessel failure in this very degenerate situation is that in which the molten mass of core material would penetrate the vessel. This subject has been reviewed quite thoroughly by a special task force headed by Ergen.¹

3.1 Sequence of Events in Reactor Accidents as Related to the Chemical Reactions

Both nuclear excursions and loss-of-coolant accidents are difficult to describe. Accident-sequence diagrams, sometimes called "accident trees" are often used to describe these accidents in a qualitative manner, and they also serve as guides for the development of the mathematical models of the accidents. Typical diagrams are shown in Figs. 3.1 and 3.2 for the nuclear excursion and the loss-of-coolant accident. It can readily be seen that even in a qualitative sense, the definition of events in a hypothetical reactor accident is difficult. Many educated assumptions have to be made regarding the sequence of these events. As stated above, the uncertainties associated with these assumptions are greater than those associated with the basic rate correlations for the metal-water reactions.

Fig. 3.1. Sequence Diagram of Nuclear-Excursion Accident. (From Ref. 85)

Fig. 3.2. Loss-of-Coolant Accident Sequence.

In both diagrams, the metal-water reaction is only one of the many factors present in a reactor accident. It must be treated as such and its relation to the other factors of the accident must be understood to assess its potential effects correctly. It can be seen that heat transfer and hydrodynamic phenomena, as well as the history of the core geometry, enter into the analysis of this reaction for a given reactor accident. It also can be seen that the energy from the metal-water reaction is not released instantaneously but over a period of time.

Some of the details regarding the accidents described in Figs. 3.1 and 3.2 are discussed later in this chapter. With the exception of the emergency core-cooling system to be used in the loss-of-coolant accident, the engineered safety features are not shown in the diagrams. Emergency core cooling must be considered in the loss-of-coolant accident sequence diagram because there is a possibility of the coolant adding to the metal-water reaction if the system does not work correctly. However, if it does work correctly, it will cool the core to below the temperatures at which any significant metal-water reaction would take place.

3.2 Analyses of the Metal-Water Reaction in Nuclear-Excursion Accidents

3.2.1 Recent Summaries and Scope of Review

The state-of-the-art for predicting the consequences of a nuclear excursion has been summarized well by Bright.⁸⁵ An earlier review directed more to fuel-pin behavior during such excursions was made by Grund.⁵⁴ Bright⁸⁵ qualitatively described this accident in the sequence diagram shown in Fig. 3.1, and Grund⁵⁴ presented a similar diagram in his report. This diagram will not be discussed in detail here because it is very complex, and Bright's article may be referred to for further information. It can be seen, however, that many factors influence the rate and the extent of the metal-water reaction during a reactor excursion accident. These include the spatial reactor core kinetics during the excursion, which determine the fission-energy input to the UO₂ fuel, the rates of transfer of this energy from the UO₂ to the metal

cladding and from the cladding to the cooling water, as well as the rate and nature of fuel pin fragmentation if it occurs. The principal concern regarding the metal-water reaction in nuclear excursions is that it may contribute to the pressure pulse generated during the excursion that could possibly be destructive to the reactor core and the primary cooling system. It is difficult to define the exact role of the metal-water reaction in this case, since the extent and nature of the pressure pulse depends on how the thermal energy deposited in the fuel pins is converted into mechanical energy and how this mechanical energy is dissipated into the reactor system. The metal-water reaction could add to the thermal energy deposited in fuel pins and generate gaseous hydrogen; however, this reaction is dependent on the cladding geometry and temperature, which are functions of the thermal-hydraulic history of the reactor core. It is difficult to separate these related variables, but there are indications that the contribution of the metal-water reaction to the potentially destructive mechanisms of the nuclear excursion is small.^{65,85,88}

To prevent destructive pressure pulses from occurring in nuclear power reactors, various devices are incorporated to limit the rate and the amount of reactivity that can be inserted into the reactor core. These include limiting the worth of any given control rod, designing reliable supports for the control rod drives and housings, etc. In addition advantage is taken of the high Doppler coefficient present in today's light-water power reactors. Design and reliability evaluations of these protective devices are beyond the scope of this report, and they will not be discussed further. Also the mechanisms for deposition of fission heat in the fuel pins and for conversion of thermal energy into mechanical energy are not covered in this review. Heat transfer effects are discussed to some extent because they influence the metal-water reaction and the fragmentation of the fuel pins. Only the fuel-pin behavior during a nuclear excursion, including the metal-water reaction, is reviewed here, although as mentioned above it is difficult to separate this from the other factors in this type of an accident.

3.2.2 Past Destructive Nuclear-Excursion Accidents

Water-moderated and -cooled reactors that have had destructive nuclear excursions are few;^{8,85} they are BORAX-1, SPERT-1, and SL-1. The nuclear excursions in BORAX-1 and SPERT-1 were intentional, while that in SL-1 was unintentional. All these reactors were small compared with present-day power reactors and had plate-type fuel elements containing highly enriched uranium-aluminum alloy fuel with aluminum cladding. The thermal lags in these fuel plates are low compared with those for the Zircaloy- or stainless steel-clad UO_2 fuel rods being used in commercial power reactors. Also, because enrichment of the uranium in power reactor fuel pins is low, there are rather sizable Doppler coefficients associated with these reactors. Because of these differences, Owens¹⁶¹ showed that the behavior of power reactors in nuclear excursions is somewhat different from that of reactors with aluminum-uranium alloy fuel plates. Therefore while the reactors with aluminum plate fuel elements can be used as general examples of nuclear-excursion accidents, the application of any data from these particular accidents to the power reactors must be done with care.

A summary of the conditions of destructive nuclear-excursion accidents is given in Table 3.1. Prior to the excursion, these reactors were not at operating power, and the cooling water in each was at ambient conditions (25°C and atmospheric pressure). The periods of the excursions varied from 2.6 msec to about 4 msec.

Table 3.1. Summary of the Destructive Nuclear Excursions in Water-Cooled Reactors with Aluminum-Uranium Cores^a.

	BORAX-1	SPERT-1	SL-1
Reactor period, sec	0.0026	0.0032	~0.004
Peak power, Mw	16,000 ^b	2,300	19,000 ^b
Nuclear energy, Mwsec	135	31	130
Chemical energy, Mwsec	Undetermined	3.5	24

^aFrom Ref. 8.

^bEstimated.

Core debris from all these reactors had similar appearance.⁸ The portions of the core that had melted had a spongy appearance, and there were considerable quantities of oxide. No attempt was made to determine the extent of the metal-water reaction in the BORAX-1 reactor, but it was determined for the other two reactors by measuring the amount of alpha alumina in the fuel debris: Alpha alumina is the aluminum reaction product formed at temperatures above 600°C. Argonne National Laboratory⁸ calculated the extent of the metal-water reactions in SPERT-1 and SL-1 by first estimating the maximum core temperature distribution during the excursion and then using these temperatures with the TREAT data shown in Fig. 2.27 to determine the amount of reaction. Their results, given in Table 3.2, agree well with the results measured by the chemical analysis of the residue from these reactors. This agreement is particularly remarkable, since the periods for the excursions in these reactors were from 2.6 to 4 msec and the periods for the TREAT excursions were from 50 to 100 msec.

Table 3.2. Metal-Water Reaction Characteristics in the Nuclear Excursions of the SL-1 and SPERT-1 Reactors^a

	SL-1	SPERT-1
Excursion parameters		
Reactor period, msec	4	3.2
Integrated power, Mwsec	130	31
Peak energy density, cal/g	500	380
Core parameters		
Aluminum present in core, kg	185	51
Uranium present in core, kg	14	4
Peak core temperature, °C	>2060 ^b	1200-1300
Percentage of core melted	32	35
Chemical parameters		
Observed chemical energy release, Mwsec	24 ± 10	3.5
Calculated chemical energy release, Mwsec	26	2

^aFrom Ref. 8.

^bVaporization temperature.

The analyses of the pressure pulses that took place during these excursions are very complex and are still under development.^{63,65,85} However, it appears at the present time that these pressure pulses were due primarily to the rate of heat transfer from the fuel to the coolant (transient boiling) and that the metal-water reaction contributed little to them.^{65,85} Much analytical and experimental work has been done by Wright^{63,65} in the development of a suitable model for the prediction of these pulses in the alloy plate reactors, but it is not sufficiently reliable to give good results. The subject of transient heat transfer has been reviewed recently by Morgan,¹⁶² who states that no complete and reliable method for predicting transient behavior of the reactor coolant is available. Morgan did, however, summarize the considerable amount of knowledge existing for this subject at the present time. Although the subject of these pressure pulses involving transient heat transfer, the conversion of thermal energy into mechanical energy, and the dissipation of this mechanical energy in the reactor system is a very difficult problem, it cannot be ignored, as was demonstrated by the SL-1 accident.

3.2.3 Nuclear Excursions in Reactors with Metal-Clad UO₂ Fuel

No reactor with metal-clad UO₂ fuel has ever experienced a destructive nuclear excursion, but a number of nondestructive nuclear-excursion tests were run in the SPERT-I reactor with an oxide core.^{86,87} This particular core was made up of stainless steel-clad UO₂ fuel pins originally used in the NS Savannah critical experiments. The neutron kinetics observed during these tests were described successfully by calculations in which use was made of the Doppler coefficient of the fuel.^{85,163} These calculational methods were extended to describe the time- and space-dependent neutron kinetic behavior of large power reactor cores in nondestructive nuclear excursions.^{85,164} Experimental data backing up these latter calculations are nonexistent, however.

The reactor manufacturers assume in their analyses that the amount of reactivity that can be inserted into power reactor cores is limited by the engineered safety features designed and built into these reactors. Based on the maximum amount of reactivity that can be inserted

into the core under these conditions, they determine the rate and the extent of the excursion by using the calculational models mentioned above. These excursions are limited by Doppler reactivity effect due to the heating of the fuel, and they are terminated by the action of the reactor safety system. Lowering of the moderator density in most cases will also help to limit the extent of the excursion, although this is often purposely neglected in the various safety analyses. The moderator density can be lowered either by the prompt heating of the water or by void generation in the water.

With the rate and the extent of the nuclear excursion known, the vendors are able to calculate the fission-energy input to the fuel. These fission-energy inputs can then be used to predict the fuel-pin behavior from calculational and/or experimental data. Most of the experimental data referenced in these safety analyses are those that were obtained in TREAT, as shown in Figs. 2.15 and 2.25. These figures show the fission-energy input required to get fragmentation of the fuel and the extent of the metal-water reaction. It should be remembered, however, that the TREAT data shown in these figures are simplified versions of a very complicated process. There are some conditions in the TREAT experiments different from those in the power reactors which could or could not have a significant effect on the fuel-pin behavior. The TREAT data were obtained from small fuel-pin specimens submerged in water in an autoclave and subjected to nuclear excursions having periods in the range 50 to 100 msec. In comparison, fuel pins in power reactors are normally in hot high-pressure flowing water, and they could possibly be subjected to periods as low as 2.7 msec.⁹⁶ It could be argued that use of the TREAT data is conservative because of the very low thermal diffusivity of the UO_2 fuel and the higher heat transfer coefficients between the fuel pin and the water in the power reactor than in the TREAT autoclave. However, other factors may be important, such as the fuel enrichment, which can influence the neutron-flux depression in the fuel and thus the average fission-energy input to the UO_2 and the reactor period, which can affect the amount of heat loss from the fuel pin to the surrounding water. Because of the importance of these data

in reactor safety, the importance of these variables should be determined. The necessary experiments are planned for the TREAT program⁴³ and the CDC-PBF program.⁵⁵

By limiting the amount of reactivity that can be inserted at any one time into power reactor cores, reactor manufacturers calculate that the fuel pins will either not be damaged or, if they are damaged, the damage will be of no consequence external to the reactor system. Within the limitations described above, these calculations appear to be reasonable. If for some unlikely reason there were larger reactivity inputs to the core, it would be possible to have excursions that could cause extensive damage to the core and possibly to the reactor primary cooling system if there were fragmentation of much of the reactor core. It is not the intent of this review to discuss the reliability of the engineered safety features designed to prevent this. Much of the information needed for predicting the consequences of the accident is unknown.^{85,88} Many factors enter into the analysis, and they are difficult or even impossible to separate and define. However, as mentioned earlier, the contribution of the metal-water reaction to the damage appears to be small.^{65,85,88}

Because of the uncertainties surrounding the assessment of the consequences of a severe nuclear excursion and because of the interest in increasing the allowable limits of the fission-energy input to the fuel pins,^{43,89} it is suggested that a strong program be undertaken to determine the consequences of nuclear excursions involving large fission-energy inputs to the fuel pins. Although the contribution of the metal-water reaction to possible damage to the reactor system may be small, other factors such as steam explosions could have serious consequences. Such a program should provide information with which to establish the allowable fission-energy inputs to the fuel in an operating power reactor. It could well be that the safety factors connected with the limits being used for present reactors are very large and could be reduced.

3.2.4 Nuclear Excursions in General Electric BWR's

In the analysis of nuclear excursions in their boiling-water reactors, General Electric assumes that the worst case is that in which

a control rod in a critical core has separated from the drive rod and has dropped freely out of the core.^{37,90} They considered earlier the case of dropping a fuel bundle into a just-critical array, but this was precluded by a refueling interlock system that prevents the necessary conditions for the accident. In all their excursion analyses, they assumed that the control rod safety system did not operate until 0.2 sec after the scram-sensing device measured 120% of the reference neutron flux. They further assumed that the excursions were limited only by the fuel Doppler coefficient, with no credit taken for the prompt heating of the moderator.

On the basis of the TREAT data shown in Fig. 2.15, the PULSTAR data,¹⁴⁴ and SPERT data, General Electric estimated that the following would happen at the various fuel enthalpies (0 cal/g UO_2 at 20°C).^{90,141,165} Perforation of the cladding would take place for enthalpies above 170 cal/g UO_2 . Fuel would start to melt at 220 cal/g UO_2 and would be fully molten at 280 cal/g UO_2 ; these data are consistent with the information shown in Fig. 2.15. Vaporization of the fuel starts to take place at 360 cal/g UO_2 when the UO_2 vapor pressure is 1 atm, and the UO_2 vapor pressure is sufficient to rupture the cladding at 425 cal/g UO_2 . Until recently General Electric limited the maximum fission-energy input to the fuel during a hypothetical nuclear excursion to a value below 280 cal/g UO_2 . Although the fuel can be partially molten and the fuel pin can fragment in this energy range, General Electric feels that this fuel breakup is gradual and the resulting pressure increases are modest.⁹⁰ Recently,⁸⁹ GE stated that a maximum fuel enthalpy of 360 cal/g could be tolerated during a nuclear excursion; that is, the enthalpy at which the UO_2 vapor pressure is just 1 atm. They thought that this was an acceptable value when consideration was given to neutron-flux depression in the fuel, heat transfer, and geometrical effects.¹⁴¹ For the Browns Ferry reactor, General Electric estimated that it would take 375 cal/g UO_2 to get deformation of the channel box sufficient to interfere with control rod motion and to cause the upper plenum head holddown bolts to yield.¹⁶⁶ They also estimated that it would take 400 cal/g UO_2 to split the fuel

channel box. They assumed that a fuel enthalpy of 425 cal/g UO_2 would be sufficient to cause prompt rupture of the cladding and that it would also make the integrity of the primary cooling system questionable. Of course the energy levels required to destroy the primary cooling system would also cause the destruction of a large part of the reactor core.

One of the analyses of the control rod drop accident in a General Electric BWR published recently is that for the Oyster Creek Nuclear Power Plant Unit No. 1 (Ref. 90). The maximum worth of a control rod when withdrawn in the normal sequence was determined to be about 1% reactivity. If for some reason the normal withdrawal procedure was not used to override the action of the control rod minimizer (a computer designed to block the withdrawal of a rod having a reactivity worth greater than 1%), the maximum control rod worth would be about 3.3%. For the very worst possible case in which a number of control rods would be withdrawn out of sequence, the maximum worth of a given control rod could be as high as 5.7%.

The control rod drop was then analyzed for three cases: (1) the reactor in a cold critical condition, (2) the reactor in a hot standby condition, and (3) the reactor operating at 10% power. It was assumed that the control rod velocity was limited by the rod velocity minimizer to 5 fps. The calculations⁹⁰ showed that the worst situation exists when the reactor is in the cold critical condition; the results for this case are shown in Fig. 3.3. If the design rod worth is 2.5% reactivity, the maximum fuel enthalpy is 250 cal/g UO_2 , which implies that part of the UO_2 melts. More detailed calculations of this case show that about 50 lb of the UO_2 in the core has peak enthalpies greater than 220 cal/g UO_2 , and therefore would melt. About 200 of the 27,440 rods in the reactor core have peak enthalpies greater than 170 cal/g UO_2 , at which value the integrity of the rod cladding is in question. The total nuclear energy release during this excursion was found to be 2500 Mwsec. For the situation in which the control rod is not withdrawn according to the normal procedure (maximum rod worth being 3.3%), the peak fuel enthalpy is about 330 cal/g UO_2 , as shown in Fig. 3.3.

Fig. 3.3. Peak Fuel Enthalpy Resulting from a Rod Drop Accident with Oyster Creek Nuclear Power Plant Unit No. 1 in the Cold Startup Condition. (From Ref. 90)

This is considered acceptable by General Electric in view of their recent position that a maximum value of 360 cal/g UO_2 could be tolerated.⁸⁹

The metal-water reaction is not mentioned in the analysis of the Oyster Creek reactor, since the fate of the reactor is believed to be primarily a function of the peak fuel enthalpy occurring during the excursion. As stated above, the contribution of the metal-water reaction to the possible destruction of the nuclear excursion is believed to be small. However, in some earlier analyses of the Dresden-3 reactor,⁹⁶ General Electric calculated as the worst case a control rod dropping out of the core while the reactor is in the hot standby condition. For a rod worth of 2.5% reactivity and a rod velocity of 5 fps, the minimum period during the reactor transient is 8.4 msec, and the peak power is 10^5 Mw. The energy release is 4000 Mwsec, of which

30 Mwsec is due to the metal-water reaction. The latter figure was derived from calculating the distribution of the peak fuel enthalpies in the core, using these enthalpies with the TREAT data shown in Fig. 2.15 to get the extent of the metal-water reaction in the various parts of the core, and multiplying these values by the heat of the reaction. It can be seen that the energy release from the metal-water reaction here is very small compared with the overall energy release. General Electric stated that the maximum fuel enthalpy for this situation is 200 cal/g UO_2 .

Dropping a fuel bundle into a just-critical array was considered for the Dresden-3 reactor because this analysis was done prior to the incorporation of the refueling interlock system into the reactor. In this study, it was assumed that the maximum worth of a fuel element added to a nearly critical core is 2.3%. It was further assumed that the initial core temperature is 68°F (20°C) and that the fuel element is dropped from a height of 2 ft above the core with an acceleration of 0.9 g. The nuclear excursion produced in this accident has a minimum period of 3.9 msec and a peak power of 1.5×10^5 Mw. The energy release of this nuclear burst is 2610 Mwsec, of which 27 Mwsec is due to the metal-water reaction. It can be seen again that the latter value, which was also calculated from the TREAT data, is small compared with the total energy release. The maximum UO_2 enthalpy in this case was found to be 200 cal/g UO_2 .

3.2.5 Nuclear Excursions in Westinghouse PWR's

Westinghouse considers six types of accidents in the nuclear excursion analyses of their pressurized-water reactors.^{36,91,92} These are (1) the startup accident caused by the withdrawal of a control rod cluster at its maximum rate, (2) the withdrawal of a control rod cluster when the reactor is at full power, (3) removal of the boron from the primary cooling water, (4) dropping a control rod, (5) control rod ejection, and (6) the fuel loading accident. In all these cases, except the control rod ejection accident, either the presence of boron in the cooling water or the reactor safety system will limit the excursion to some point below which the departure from nucleate boiling occurs.

If departure from nucleate boiling is prevented, Westinghouse indicates that the fuel-pin integrity is preserved and that no metal-water reaction takes place. Since the reliability of the reactor safety systems is beyond the scope of this report, no more will be said of them here, except that if they fail to work when needed, departure from nucleate boiling could possibly take place.

The only case in which departure from nucleate boiling could possibly occur is a nuclear excursion due to the ejection of a control rod. For this situation, Westinghouse uses the criterion that there will be no further damage to the primary cooling system.⁹¹ If fuel melting is prevented during the excursion, the fuel-cladding configuration will be kept intact. The rate of heat transfer is then limited by the low surface-to-volume ratio, and detailed computer analyses show that the pressure surge generated during the excursion is not sufficient to cause any further damage to the primary cooling system.⁹² If it is shown that there is a possibility of melting and fragmenting the fuel in this power burst, Westinghouse indicates that they will make a detailed analysis of the reactor to demonstrate that this will not dissipate energy into the water rapidly enough to create a pressure surge capable of violating the integrity of the remaining primary cooling system or of the adjacent fuel.^{36,91} They gave further support to this argument from the results of a preliminary analysis which showed that the reactor system components would not exceed their yield stress if some fuel were dispersed into the water.³⁴ In this case 10-mil-diam high-density fuel particles from 25 fuel rods are dispersed into the water in a "typical pressurized water reactor."

Westinghouse⁹⁸ has stated further that there would be no expulsion of fuel into the coolant unless the peak enthalpy of the fuel was such that the fuel was in its fully molten condition. They assume that the fuel will start to melt when its enthalpy is 247 cal/g UO_2 and that the heat of fusion is 66 cal/g UO_2 . The 247 cal/g UO_2 value appears to be a little higher than the values given in Fig. 2.15. The argument they give in support of this reasoning is that until all the fuel has become molten, a liner of a crucible of solid UO_2 is maintained between that

portion of the UO_2 that is melted and the relatively cool cladding during a nuclear transient.¹⁶⁷⁻¹⁶⁹ They also interpret the results from the TREAT studies of Liimatainen and his associates^{49-51,150} to be that the most likely mechanism for the fuel-pin failure and the release of the UO_2 into the coolant is the buildup of a high internal pressure because of the boiling of the oxide fuel. They make no mention in their reports of any metal-water reaction during the nuclear power bursts and thus assume that the contribution of this reaction to the consequences of this accident is negligible.

Detailed calculations regarding the consequences of a control rod ejection accident in the San Onofre reactor were reported recently by Westinghouse.⁹² This accident was analyzed for both the no-power and the full-power situations at both the beginning of core life and at the end of core life. The temperatures of fuel and cladding during the power burst were determined from the CHIC-KIN program written by Redfield.¹⁷⁰ This program makes simultaneous use of both reactor kinetics relations and basic hydrodynamic conservation relations. It is assumed that the rod geometry remains intact during the transient, but that subcooled boiling could occur. For this particular study, the fuel was divided into eight radial increments with a ninth radial increment for the cladding. The contact heat transfer coefficient between the fuel and the cladding was assumed to be $2000 \text{ Btu/hr}\cdot\text{ft}^2\cdot^\circ\text{F}$. The worst case was found to be for the no-power situation at the end of core life in which the worth of the ejected rod is 0.8% reactivity. Even for this case, the maximum fuel temperature at the hot spot was determined to be 2240°C , which is below the melting point of the UO_2 . Eleven percent of the fuel pins experienced departure from nucleate boiling, and only 1% of the fuel had temperatures greater than 1600°C . The maximum pressure generated in the primary cooling system as a result of the increase of the heat flux through the cladding during the excursion accident was found to be less than 2316 psia, and it occurred 9.7 sec after initiation of the nuclear power burst. This is below the 2500-psia design pressure of the reactor.

3.2.6 Nuclear Excursions in Babcock & Wilcox PWR's

Babcock & Wilcox⁹³ also consider a number of situations in which nuclear excursions can occur in their pressurized-water reactors. They were able to calculate that power bursts initiated by uncontrolled rod withdrawal could be terminated without damage to the core or the primary cooling system. Refueling accidents are precluded by adding boron to the moderator water. Therefore the only situation in which the integrity of the primary cooling system might be questionable is that due to the ejection of a control rod. Like the other vendors, Babcock & Wilcox use the criterion that no further damage will be done to the primary cooling system in case such a rod is ejected.

They state that fuel melting would start at UO_2 enthalpy values of 220 to 225 cal/g, which is consistent with the information shown in Fig. 2.15. They also state that the heat of fusion of UO_2 is 60 cal/g, which is also consistent with the other data. The vapor pressure of UO_2 at 325 cal/g is 14.7 psia, and at 420 cal/g it is sufficient to burst fresh Zircaloy cladding. However, Babcock & Wilcox point out that the cladding failure of UO_2 is dependent on the fission-product gas pressure, irradiation of the fuel and the cladding, and possible zirconium hydriding. Therefore they chose a value of 285 cal/g UO_2 (all the fuel is molten) at which the fuel cladding would burst and put the integrity of the primary cooling system in question. They also assumed that the cladding of the fuel rods that experience departure from nucleate boiling would fail but would not result in any question regarding integrity of the primary cooling system. The metal-water reaction was included in their calculations, and the extent of this reaction was determined from the following correlation of the TREAT data shown in Fig. 2.15:

$$\text{Metal-water reaction (\%)} = 0.125 (\text{Final fuel enthalpy} - 125) ,$$

where the final fuel enthalpy is the sum of the initial fuel enthalpy and the fuel enthalpy produced by the nuclear burst in calories per gram of UO_2 based on a reference temperature of 20°C. This relation implies that the metal-water reaction could occur for fuel enthalpies

as low as 125 cal/g UO_2 , which appears conservative in view of the data shown in Fig. 2.15. They further assumed that departure from nucleate boiling occurred at a heat flux of 6.36×10^5 Btu/hr·ft², which is equivalent to a fuel enthalpy of 140 cal/g UO_2 at the end of core life (EOL) and 130 cal/g UO_2 at the beginning of core life (BOL).

The rod-ejection accident was analyzed for the Oconee Power Station⁹³ by using an analog point-kinetics model that gave results which compared favorably with the results predicted by the WIGL2 digital computer program.¹⁷¹ Babcock & Wilcox considered this situation for both the reactor initially at its source power and its full power. They found for a reactor at 10^{-9} of its full power and 0.5% $\Delta k/k$ subcritical, a rod worth 1% $\Delta k/k$ ejected in 150 msec resulted in an excursion with a peak power of 39% of the full reactor power. A low-pressure signal trips the safety rods 1.7 sec after the ejection starts. The peak power is reached about 15 sec after the rod is ejected because of Doppler feedback controlling the rate of rise of the neutron power. In this case the peak fuel temperature is reported to be 482°C, which is far below the temperature where fuel damage or metal-water reaction can take place.

The percentages of the core that would experience departure from nucleate boiling and the zirconium that would react with the water were calculated for nuclear power bursts initiated at full-power conditions with the rod being ejected in 150 msec and the safety rods tripping 0.3 sec after the excursion. Results of these calculations are shown in Figs. 3.4 and 3.5. Babcock & Wilcox⁹³ estimated that a conservative maximum control rod worth for this type of an accident is 0.2% $\Delta k/k$. At the beginning of core life, it can be seen that there is no departure from nucleate boiling and virtually no metal-water reaction. They reported that the peak enthalpy in the hot fuel rod is about 130 cal/g UO_2 .

At the end of the core life, about 10% of the core would experience departure from nucleate boiling, and 0.4% of the zirconium would react with water. They estimate that the total fission energy produced during the burst is 2500 Mwsec and that the energy contributed by the

Fig. 3.4. Percentage of Core Experiencing Departure from Nucleate Boiling (DNB) as a Function of Ejected Control Rod Worth at Full Power for the Oconee PWR. (From Ref. 93)

metal-water reaction is 510 Mwsec. The latter value is probably conservative because of the pessimistic nature of the metal-water correlation used by Babcock & Wilcox. The peak enthalpy of the nominal fuel rod is 112 cal/g UO_2 and that of the hot rod is 157 cal/g UO_2 . These values are below the range where fuel melting occurs.

In none of these cases do damaging pressure pulses occur. Therefore, according to Babcock & Wilcox calculations, the criterion of no further damage to the primary cooling system has been met.

Fig. 3.5. Zirconium-Water Reaction as a Function of Ejected Control Rod Worth at Full Power for the Oconee PWR. (From Ref. 93)

3.2.7 Nuclear Excursions in Combustion Engineering PWR's

Combustion Engineering considers six types of nuclear excursion accidents in the safety analyses of their pressurized-water reactors.^{94,95} These are (1) the startup accident caused by the continuous withdrawal of a group of control rods, (2) a core barrel failure where the core falls down a short distance into the reactor vessel, (3) the dilution of the boron in the coolant water or the injection of cold water into the primary coolant, (4) the withdrawal of the control rods while the reactor is at power, (5) a control rod drop, and (6) the ejection of a control rod from the reactor vessel. In all cases, with the exception of the control rod ejection accident, they were able to calculate that the fuel-pin temperatures in the Palisades Power Plant did not reach the point at which departure from nucleate boiling occurred.

For the case of a control rod ejection accident in the Palisades Plant,⁹⁵ Combustion Engineering used the criteria that no additional

damage to the primary cooling system would take place because of the nuclear excursion and that the power burst would not result in damage to the core such that it could not be cooled after the excursion. Like Westinghouse, they used the CHIC-KIN program¹⁷⁰ to obtain the fuel-pin temperatures during the accident. For adiabatic heating of the fuel and a UO_2 melting point of 2800°C , they calculated that 0.4% of the fuel melted if the ejection of a control rod took place while the reactor was at full power (0.4% rod worth) and that 3.61% of the fuel melted while the reactor was at temperature but at zero power (1.0% rod worth). The Doppler coefficient limited the excursion 0.1 sec after the ejection of the control rod, since the safety rods would not start moving into the core until 4 sec after the start of the rod ejection.

To get rupture of the pressure vessel, Combustion Engineering estimated at least 20% of the core would have to melt during the control rod ejection accident. (They make no mention of the possibility of shearing off the primary coolant pipes from the pressure vessel.) They assumed that the molten fuel would disperse into the fuel in the form of 10-mil-diam droplets, and they determined the rate of heat transfer to the coolant from the molten fuel by using a simple computer code that includes the effect of the steam film blanketing the molten UO_2 droplets. They also mentioned that the energy from the metal-water reaction determined from the results of the TREAT studies of Liimatainen and his associates^{49-51,150} was included in their calculations. However, they did not give any specific details on how this was included.

3.2.8 General Comments Regarding Vendors' Analyses of Nuclear Excursions

It can be seen above that all the reactor vendors use the criteria in their assessments of nuclear excursions that no damage or additional damage (in case of the rod ejection accident) is done to the primary cooling system and that the excursion will not result in damage to the core such that it cannot be cooled after the excursion. If the fuel pins do not fragment during the power burst, it can be shown that these criteria can be met readily. Sometimes it is shown that the excursion lacks sufficient energy input to the fuel pins to even melt any of the

fuel, and thus the fuel pins retain their general shape and form. As shown in Fig. 2.15 the fuel pins remain intact until most of the fuel melts, and many of the reactor manufacturers argue that they do not fragment until all the fuel is molten. At fission-energy inputs greater than the amount required to melt the fuel, the pins certainly fragment. Many of the vendors state that as long as the UO_2 does not vaporize, the pressure pulse resulting from the power burst involving the fragmentation of the fuel pins is not sufficient to violate the criteria stated above. They argue that the rate of transfer of the heat from the fragments is sufficiently slow to prevent a sudden pressure burst. Because of this it has been stated that nuclear power bursts resulting in a fuel peak enthalpy of 360 cal/g UO_2 could be tolerated. However, as recently demonstrated by Ivins,⁴³ fission-energy inputs of this magnitude can cause severe pressure pulses. More work is necessary to understand the effect of a fragmenting fuel pin on the adjacent fuel pins and on the reactor primary cooling system. This is a very complicated subject that involves the conversion of the thermal energy into mechanical energy and the dissipation of this mechanical energy in the reactor system.

The role of the metal-water reaction in these excursions appears to be secondary, and the reactor manufacturers usually so state in their safety analysis reports or do not mention it at all. If the fuel pins do not fragment, it can be seen in Fig. 2.15 that the extent of reaction is small. At higher fuel enthalpies, the energy produced by the metal-water reaction is small compared with the nuclear energy required to get to these fuel enthalpies. Because of this, the analytical approaches in assessing the consequences of this type of accident are thermal-hydraulic in nature and involve the transfer of sensible heat from fuel pins and their fragments rather than metal-water reaction energy.

3.3 Analyses of the Metal-Water Reaction in Loss-of-Coolant Accidents

3.3.1 Introduction and Previous Summaries

It is assumed in the safety analyses of the power reactors that the engineered safety features in the reactor prevent the rupture of the

primary cooling system during a nuclear excursion. However, the reactor manufacturers do consider the possibility of the initiation of an accident by the rupture of a pipe in the primary cooling system. The size of this rupture can vary from a very small leak to the double-ended failure of the largest pipe in the primary cooling system. Failure of the reactor pressure vessel is assumed to be incredible at the present time.* If at some later date this is considered credible, it will have a major influence in the nature of the accident, as will be seen later. A recent review of this accident, which is termed a loss-of-coolant accident, and methods of preventing it or coping with it was made by a special task force headed by Ergen.¹ Earlier reviews were made by Morrison and his associates,¹⁰⁵ Jensen,¹⁰³ and Wilson.¹⁷²

The definition of this accident, which is described in Fig. 3.2, is also quite complicated, as is the definition of the nuclear-excursion accident. It will be seen later that unknowns regarding the prediction of the effect of the metal-water reaction in a loss-of-coolant accident are more related to the definition of the sequence of events and their mathematical simulation than to the basic metal-water reaction data. It is generally assumed that following a rupture in the primary cooling system, the cooling water is blown down from the reactor system until the pressures in the primary cooling system and the containment vessel reach equilibrium. It is assumed further that during this blowdown process the reactor becomes subcritical by void formation and removal of water from the reactor core and/or by insertion of poison into the reactor core. The poison may be control rods or a boron solution. The amount of water left in the pressure vessel following the blowdown is dependent on the rate and the nature of the cooling system rupture. For large double-ended pipe breaks, it is conceivable that very little water is left in the pressure vessel. The amount of water left in this vessel is important because it is the source of steam for the possible metal-water reaction in the reactor core.

*This assumption has, on occasion, been questioned. See letter from W. D. Manly, Advisory Committee on Reactor Safeguards, to G. T. Seaborg, USAEC, Nov. 24, 1965; included in USAEC press release, H-262, Dec. 3, 1965.

Following the coolant blowdown, the fuel and the cladding heat up due to the delayed fissions and the decay of the fission products. As the cladding reaches higher temperatures (1000 to 1200°C), it reacts with any steam flowing into the core region, such as that generated by the boiling of the water remaining in the bottom of the reactor vessel. This provides an additional heat source in the reactor core. Hydrogen is generated by the metal-water reaction, and it could react with the air in the containment vessel. If it did, the hydrogen-air reaction could compromise the integrity of the containment vessel. Unless core heatup was checked by some method, such as operation of an emergency core-cooling system, it is likely that the fuel pins would fragment and/or melt and fall to the bottom of the pressure vessel.¹ It is also likely that this melted core would be able to penetrate the pressure vessel wall and pass into the containment vessel. Just what the nature or the state of this molten material would be before and after it had penetrated the pressure vessel is uncertain. However, as mentioned before, it can be conjectured that the containment vessel could fail by a simple melt-through of the molten core, by shock waves generated by steam explosions or the hydrogen-air reaction, or by the buildup of hydrogen pressure due to the metal-water reaction taking place over a long period of time. In this extremely degenerate situation, fission products could be released to the containment vessel and the surrounding environs. Much of the information regarding the events described above is beyond the scope of this report, but the events are mentioned in order to give some idea of where the metal-water reaction fits into the description of reactor accidents.

It was stated above that most of these events can be prevented and/or minimized by operation of emergency core-cooling systems. These systems, which would start to operate immediately after initiation of a break in the primary cooling system, have been reviewed in detail by Lawson.² Because many events in a reactor accident have a great influence on the nature of the metal-water reaction and are also important in the design of the emergency core-cooling systems, there is some overlap of the information presented in Lawson's paper and in this report. However, this overlap is minimized as much as possible.

3.3.2 Geometrical and Other Characteristics of Power and LOFT Reactors

Before continuing with discussions of the loss-of-coolant accident, it is necessary to review the geometrical and operating characteristics of the various reactors. It may be seen that the rate and extent of any chemical reactions in this type of accident are dependent on the thermal and hydraulic histories of the accident. These in turn are dependent on the geometrical and other operating characteristics of the reactor. In addition to the power reactors, characteristics of the LOFT reactor are given because this reactor is designed for intentional loss-of-coolant accident studies. The original plan for this reactor was to intentionally rupture the primary cooling system and allow the reactor core to melt down.^{173,174} However the LOFT program has been reoriented to first investigate the effectiveness of the emergency core-cooling systems because of their importance to reactor safety.¹⁷⁵

The general arrangements of typical reactor vessels and core components being built by the four light-water reactor manufacturers are shown in Figs. 3.6 through 3.9. Other characteristics of these reactors are listed in Table 3.3. All the PWR reactor vessels and cores are quite similar and have open-lattice cores. The control rods of both Westinghouse and Babcock & Wilcox reactors are in clusters inserted in small stainless steel thimbles located in the fuel elements, as can be seen in Figs. 3.6 and 3.7. The Combustion Engineering reactor has cruciform control rods, as shown in Fig. 3.8. The General Electric BWR reactor vessel and core arrangement are of course somewhat different, as shown in Figs. 3.9 and 3.10. In these reactors, there is a steam dome at the top of the reactor vessel, and the control rod drives are located at the bottom of the vessel. The fuel elements have shrouds, as shown in Fig. 3.10, and the control rods are of the cruciform design.

The LOFT reactor, shown in Figs. 3.11 and 3.12, is a 50-Mw PWR and is a much smaller reactor than the commercial power reactors. However, power densities in this reactor are similar to those of some commercial reactors. The fuel element, shown in Fig. 3.12, has a vented stainless steel shroud, and its active length is 3 ft, which is less than the 12-ft

Fig. 3.6. Westinghouse PWR Reactor Vessel and Internals. (From Refs. 36 and 91)

Fig. 3.7. Babcock & Wilcox PWR Reactor Vessel and Internals. (From Ref. 93)

Fig. 3.8. Combustion Engineering PWR Reactor Vessel and Internals.
(From Ref. 94)

Fig. 3.9. General Electric BWR Reactor Vessel and Internals. (From Refs. 37 and 96)

Table 3.3. Summary of the Characteristics of Some Typical Power Reactors and LOFT

Reactor	Turkey Point 3 and 4	Indian Point 2	Oconee 1 and 2	Palisades	Dresden 3	Browns Ferry	LOFT
Type	PWR	PWR	PWR	PWR	BWR	BWR	PWR
Manufacturer	Westinghouse	Westinghouse	Babcock & Wilcox	Combustion Engineering	General Electric	General Electric	
Thermal power rating, Mw	2,097	2,758	2,452	2,200	2,255	3,293	50
Reactor core characteristics							
Active length, in.	144	144	144	132	144	144	36
Effective diameter, in.	119.5	133.7	128.9	136.6	182.2	187.2	41.5
Number of fuel pins	32,028	39,372	36,816	44,223	35,476	37,436	3,292
Fuel material	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂
Cladding material	Zircaloy	Zircaloy	Zircaloy-4	Zircaloy-4	Zircaloy-2 ^a	Zircaloy-2 ^a	Zircaloy-4
Fuel pin diameter, in.	0.422	0.422	0.420	0.413	0.570	0.562	0.413
Cladding thickness, in.	0.0243	0.0243	0.026	0.024	0.036	0.032	0.025
Fuel pellet diameter, in.	0.3669	0.3669	0.362	0.359	0.488	0.488	0.357
Rod spacing (square pitch), in.	0.563	0.556	0.558	0.553	0.738	0.738	0.580
Control rod type	Rod cluster	Rod cluster	Rod cluster	Cruciform	Cruciform	Cruciform	Cruciform
Control rod material	5% Cd-15% In-80% Ag, type 304 stainless steel cladding	Same	Cd-In-Ag, type 304 stainless steel cladding	B ₄ C sheathed in stainless steel	B ₄ C sheathed in stainless steel	B ₄ C sheathed in stainless steel	Boron-stainless steel alloy (1.75 wt % ¹⁰ B), Zircaloy-2 follower
Thermal and hydraulic characteristics							
Fraction of heat generation in fuel	0.974	0.974	0.973	0.975	0.960	0.960	(b)
Power density, w/cm ³	79.3	83.3	79.6	69.4	36.7	50.8	62
Average specific power, kw/ft of rod	5.3	5.7	5.4	4.41	5.09	7.04	5.20 ^b
Maximum specific power, kw/ft of rod	17.3 (19.3) ^c	18.5 (20.7) ^c	17.49	14.55	15.3	18.3	17.6 ^b
Average heat flux, Btu/hr·ft ²	1.64 × 10 ⁵	1.76 × 10 ⁵	1.68 × 10 ⁵	1.39 × 10 ⁵	1.16 × 10 ⁵	1.63 × 10 ⁵	1.51 × 10 ⁵
Peak-to-average heat flux ratio	3.25	3.25	3.15	3.30	3.00	2.60	3.40
Primary coolant pressure, psig	2,235	2,235	2,185	2,085	1,000	1,000	2,330
Average primary coolant temperature, °F	574	570	579	568	543	543	543
Average cladding temperature, °F					558	558	627
Average fuel temperature, °F	1150		1385	1100	1000	1100	1236
References	91	36	93	94	96	37	172, 174, 176

^aFuel element shroud is Zircaloy-4.^bIt is assumed that 97.5% of reactor heat will be generated in fuel.^cAt maximum overpower.

Fig. 3.10. General Electric BWR Fuel Assembly. (From Refs. 37 and 96)

Fig. 3.11. Cross-Sectional View of LOFT Reactor. (From Ref. 174)

Fig. 3.12. LOFT Reactor Fuel Element. (From Ref. 174)

value typical of the present power reactors. Cruciform control rods containing a stainless steel-boron alloy are used.

Because of these differences, comparison of results for the various reactors must be done with care. It will be seen later that much has been done about predicting the consequences of the intentional loss-of-coolant accident in LOFT. However, factors such as the active rod length and the difference in fuel element geometry could influence the consequences of such an accident. Also it should be remembered that the PWR cores are open liquid-phase systems, whereas the BWR cores are shrouded mixed-phase systems. The sizes of the primary coolant piping containing the liquid phase differ for the various reactors. This also could influence the rate of coolant blowdown and thus the rate of core heatup.

3.3.3 Early Analyses of the Metal-Water Reaction in Loss-of-Coolant Accidents

In the analysis of the metal-water reaction in this type of an accident, two of the earliest and often referenced works are those of Lustman¹¹⁸ and of Owens and his associates.¹⁷⁷ Both these documents show that the metal-water reaction is a significant source of energy in a loss-of-coolant accident but would not cause catastrophic events. Owens and his co-workers also pointed out the importance of the heat transfer and flow characteristics in a reactor core with respect to the rate and the amount of the metal-water reaction. Since the time these

studies were completed, the size and amount of metal in power reactors have increased greatly. However, with the aid of much improved computer technology, analytical techniques have become much more sophisticated and have given a more accurate picture of the role of the metal-water reaction in the loss-of-coolant accident.

3.3.4 Coolant Blowdown and Heat Transfer

In analyses of hypothetical loss-of-coolant accidents, it has been found that the state of the reactor at the end of the blowdown phase has a large influence on the nature of any metal-water reaction that takes place during the following core heatup.^{103,108,109,178,179} For large breaks in the primary cooling system, essentially no metal-water reaction can take place at least during the initial part of the blowdown because of the cooling effect of the water passing rapidly through the core. Because of the strong effect of coolant blowdown on subsequent core heatup and because of possible structural damage to reactor internals, much attention has been given to coolant behavior during this phase of the accident. However, little experimental information has been obtained regarding coolant heat transfer coefficients during blowdown. About the only data reported in the literature are those supplied by General Electric in the Dresden-3 preliminary design and safety analysis report.¹⁰⁴ Since coolant behavior and heat transfer during blowdown are beyond the scope of this report, they are discussed here only to the extent necessary to give an indication of effects on the metal-water reaction. They are covered to some extent by Lawson² in his paper on emergency core-cooling systems.

A number of experimental programs have been conducted or are being considered to determine water behavior during blowdown from PWR's and BWR's. These programs include the LOFT semiscale tests,^{106,180,181} tests being performed by the UKAEA,³ water decompression tests of the Illinois Institute of Technology Research Institute,^{100,182} Containment Systems Experiment blowdown tests,¹⁰⁰ and tests by General Electric.^{104,183} Redfield and his associates¹⁸⁴ reported blowdown characteristics of the coolant following rupture of a small pressurized-water loop. All these

tests indicated that coolant blowdown behavior could be described by four definite time phases. These are, in order (1) a subcooled phase in which acoustic effects predominate mainly in the liquid phase, (2) a metastable transition phase in which nucleation and initial growth of vapor bubbles occur along with initial fluid expansion and extremely low acoustic velocities, (3) a forced-convection phase with two-phase fluid behavior predominating, and (4) a natural-convection phase with the steam boiloff mechanism predominating.

Many programs have been written for analyzing coolant blowdown, and many of them have been summarized by Ergen,¹ by Waage,¹⁰¹ and by Morrison and his associates.^{100,105} A number of these programs were tabulated by Waage,¹⁰¹ and Tables 3.4 and 3.5 are slightly modified versions of his tables. It can be seen readily that a number of factors enter into these codes, and there must be compromises and simplifying assumptions in order for the computer running times to remain reasonable.^{101,185} The first three codes listed in these tables, BURST, SATAN, and WATER HAMMER, calculate primarily the decompression of the water during the subcooled portion of the blowdown in pressurized-water reactors. The effects of the decompression wave are included, and therefore these codes are more complicated than the others. The remaining codes are directed more to the saturated portion of coolant blowdown.

When the results of these codes are compared with the data obtained in the LOFT semiscale blowdown tests, they generally predict the pressure history in the pressure vessel quite well but are much in error in predicting the amount of water left in the vessel. This is important for the metal-water reaction, since this water is the source of steam for the reaction. Also in programs such as BURST, quite sizable pressure oscillations across the reactor core have been predicted to occur during the subcooled portion of the blowdown. However, later tests in the LOFT semiscale facility containing mockup cores showed that such oscillations are severely damped and do not produce significant loading on reactor cores.¹⁰² This is important to the nature of any metal-water reaction in a loss-of-coolant accident, since it is dependent on steam flow which, in turn, is dependent on core geometry.

Table 3.4. Coolant System Features of Blowdown Computer Programs

	Computer Program						
	BURST ¹⁸⁶	SATAN ¹⁸⁷	WATER HAMMER ¹⁸⁸	RELAPSE ¹⁸⁹ (FLASH ¹⁹⁰)	LOCO ¹⁹¹	RIP ¹⁸³	K.E.. ¹⁹² SAT.
Distributed (D) or lumped (L) model	D	D	D	L	L	L	D
Subcooled (S) and/or two-phase (2-P) properties	Both	Both	S	Both	Both	Both	2-P
Sonic effects	Yes	Yes	Yes	No	No	No	No
Slip (S) or homogeneous (H) flow	H	S	H	H		H	H
Free liquid surface	No	No	No	Yes	Yes	Yes	No
Portion of blowdown treated	~1 sec	All	~1 sec	All	All	All ^a	Saturated only
Pipe and vessel heat capacity	No	No	No	No	Yes	No	Yes
Separate pressurizer	No	Yes	Yes	Yes	Yes	No ^a	Yes
Number of nodes	≤4000	≤70	100	3	1-2	5	53

^aFor boiling-water reactors.

Table 3.5. Core and Leakage Features of Blowdown Computer Programs

	Computer Program						
	BURST ¹⁸⁶	SATAN ¹⁸⁷	WATER HAMMER ¹⁸⁸	RELAPSE ¹⁸⁹ (FLASH ¹⁹⁰)	LOCO ¹⁹¹	RIP ¹⁸³	K.E. ¹⁹² SAT.
Reactor kinetics	No	No	No	Yes ^a	No	No ^b	No
Core decay heat	No	Input	No	Yes	Input	Input	Yes
Core heat capacity	No	Yes	No	Yes	Yes	No ^b	Yes
DNB model	No	No	No	Yes	No	No ^b	No
Emergency core coolant	No	No	No	Yes	Yes	No	No
Leak flow model ^c	P	N	F	M	F	M	F
Variable leak initiation	Yes	Yes	Yes	Yes	No	No	No

^aRELAPSE is an improved version of FLASH that incorporates a neutron kinetics routine to permit its use in power-transient analyses, such as for the rod-ejection accident.¹⁸⁹

^bProgram used for boiling-water reactors only; use of test information as input data to RIP precludes need for these features.

^cF, Fauske model;¹⁹³ M, Moody model;¹⁹⁴ N, Nahavandi's modification of Fauske and Moody models; P, exit pressure model.

The blowdown times for PWR's and BWR's are of course different. (This should not be construed as a merit of one reactor over another.) The PWR's contain highly pressurized subcooled-liquid systems (with the exception of the pressurizers), and it is postulated that there could be a double-ended failure of the large primary coolant piping. In contrast, BWR's are larger systems that operate at lower pressures with both liquid and gas phases. For these reactors, it is postulated that the break for the maximum credible accident is a double-ended failure of a recirculating line, with the critical flow area being the sum of the jet-pump inlet-nozzle, suction-nozzle, and equalizing-line areas. This total area is smaller than that available in the double-ended pipe failure in a PWR. Westinghouse⁹⁸ states that the blowdown time following a failure of the largest pipe in their PWR is about 13 sec, with about 6 sec required to uncover the top of the core and about an additional 1 sec to uncover the bottom of the core. They calculate that very little water is left in the pressure vessel after the blowdown. Failure of smaller pipes would, of course, result in longer blowdown times. Babcock & Wilcox⁹³ calculated similar results with a modified version of the FLASH code. Combustion Engineering⁹⁴ calculated a blowdown time of only 5 sec, but their analysis appears to be somewhat simplified. General Electric^{37,96} calculated 24- to 30-sec blowdown times in their reactors, with subcooled liquid flowing out of the recirculation lines during the first 4 sec and a two-phase mixture flowing out during the rest of the blowdown.

As may be seen, much has gone into the development of an accurate picture of the coolant blowdown resulting from a double-ended failure of any pipe in the primary cooling system. There is some effort being given to determining the nature of a pipe break,¹⁹⁵ and this should be stressed more in the future, since it could have a large influence on the blowdown and the rest of the accident, including the metal-water reaction.

As mentioned above, little experimental information is available regarding core heat transfer during the blowdown period. Blowdown heat transfer coefficients typical of those used by General Electric, based on their experimental data, are shown in Fig. 3.13. Westinghouse¹⁹⁶

Fig. 3.13. Blowdown Heat Transfer Coefficients Used in the Design Break for Dresden 3 Reactor. (From Ref. 104)

blowdown calculations are based on the assumption that nucleate boiling heat transfer occurs until departure from nucleate boiling is reached, at which time heat transfer by stable film boiling is assumed. After the time when the fuel-pin surface is uncovered until it is covered again by the water from the emergency core-cooling system, the heat is removed by the steam flowing through the reactor core. Babcock & Wilcox⁹³ do essentially the same thing by assuming nucleate boiling heat transfer until departure from nucleate boiling is reached and then film boiling having a coefficient described by a modified version of the Seider-Tate

equation. There is no published information on what Combustion Engineering assumes for these coefficients.

Some idea of the effect of the blowdown heat transfer coefficient on fuel-pin temperatures of LOFT was obtained by Jensen.¹⁰³ Results of his study, shown in Fig. 3.14, indicate that the fuel-pin temperatures vary considerably with the assumed blowdown coefficient. This can have a great bearing on the nature of the metal-water reaction during a loss-of-coolant accident, since the state of the core at the end of blowdown pretty much sets the stage for the rest of the events during the accident. It can be seen that more work is required to get better values of these coefficients.

3.3.5 Metal-Water Reaction During Reactor Core Heatup

During and after coolant blowdown, the fuel in the reactor core will start to heat up due to fissions from the delayed neutrons and the decay of the fission products. Unless checked by an emergency core-cooling system, the fuel pins can heat up to temperatures at which the cladding can react with any steam passing through the core region. The source of this steam is the boiling of the water remaining in the pressure vessel during and/or after coolant blowdown. As mentioned before, the discussion regarding the emergency core-cooling systems is kept as limited as possible here because these systems are being reviewed by Lawson.²

Computer Programs for Analyzing Reactor Core Heatup. A number of digital computer programs describing reactor core heatup following coolant blowdown have been written. Many of these have been summarized by Ergen¹ and by Waage,¹⁰¹ and they are listed in Tables 3.6 and 3.7, which are slightly modified versions of the tables in Refs. 1 and 101. Like the coolant blowdown, the core heatup is a complex process, and simplifications have to be made in these programs in order to keep the computer running times reasonable. Experimental information obtained up to the present time has been incorporated into these programs, but there are still some gaps in the data and assumptions have to be made. This is particularly true above the point where the cladding has reached

(a)

(b)

(c)

Fig. 3.14. LOFT Fuel-Pin Temperatures During Blowdown Phase as a Function of Heat Transfer Coefficients. (From Ref. 103)

Table 3.6. Geometry and Heat Transfer Features of Core-Heatup Computer Programs

	Computer Program					
	LOCTA-R ⁹¹	TACT-V ¹⁰⁴	NURLOC ^{105,197}	ARC-II ^{176,189}	MOXY-II ^{106,180}	CHEMLOC-II ^{107,109}
Originating organization	Westinghouse Atomic Power Division	General Electric Atomic Power Equipment Division	Battelle Memorial Institute	Phillips Petroleum Company	Phillips Petroleum Company	Argonne National Laboratory
Type of geometry	Radial and axial	Radial and axial	Annular ring	Annular ring	Quarter core: x-y	Radial and axial
Maximum number of nodes	60	1250	3500	350	460	2500
Part of system represented	Core fuel	Core	Vessel and core	Vessel and core	Vessel and core	Core
Conductive heat transfer	Yes	Yes	Yes	No	No	Yes
Radiative heat transfer	Yes	Yes	Yes	Yes	Yes	Yes
Reflectivity	Yes	Yes	No	Yes	Yes	Yes
View factors	Supplied as input	Supplied as input	Internally calculated	Supplied as input	Supplied as input	Supplied as input
Type of solution of conduction equation	Explicit	Explicit	Explicit	Explicit	Lumped explicit	Explicit

Table 3.7. Zirconium-Steam Reaction and Disassembly Features of Core-Heatup Computer Programs

	Computer Program					
	LOCTA-R ⁹¹	TACT-V ¹⁰⁴	NURLOC ^{105, 197}	ARC-II ^{176, 189}	MOXY-II ^{106, 180}	CHEMLOC-II ^{107, 109}
Zirconium-steam reaction	Parabolic ^a	Parabolic ^a	Parabolic ^a	Parabolic ^a	Parabolic ^a	Parabolic ^a
Steam limiting	Yes	No	Yes	Yes	Yes	Yes
Cladding melting (heat of fusion)	Yes	Yes	No	Yes	No	Yes
Fuel melting (heat of fusion)	No	No	No	Yes	No	Yes
Core migration	Cladding only	Cladding only	Yes	No	No	Yes
Emergency coolant injection	Yes	Can specify h ^b	Can specify h ^b	No	No	No
Steam flow circulation	Supplied as input	No	Internally computed	Internally computed	Supplied as input	Supplied as input

^aBaker and Just's relation.⁴¹

^bFilm heat transfer coefficient.

the melting temperature. Prior to any melting of the fuel pins, these programs are basically heat balances on the fuel pins remaining in their original geometry. No allowance is made for the possibility that the fuel rods may bow or swell. Just how important particular geometrical changes are is uncertain, but General Electric¹³⁴ indicates that they have no great bearing on the overall safety of the reactor. However, tests and calculations supporting this statement have not yet been documented. All these programs, except TACT-V, describe the metal-water reaction as the minimum predicted by Baker and Just's parabolic relation⁴¹ or by the availability of the steam to the core. For the TACT-V program, an unlimited steam supply for this reaction is assumed, and therefore the program simply describes it by Baker and Just's relation.¹⁰⁴ In the NURLOC and CHEMLOC programs, an additional limitation for the metal-water reaction is included;^{105,107,110,197} that is, the rate of diffusion of the steam to the cladding surface is limited by the diffusion resistance of the hydrogen-steam film adjacent to the cladding.

The NURLOC, ARC, MOXY, and CHEMLOC programs are directed in part to the analysis of reactor cores in a loss-of-coolant accident without emergency core cooling. Because of this they incorporate factors such as radiant heat transfer to the core barrel and the reactor vessel and axial heat conductance in the fuel pins, which are important over the longer time periods. The LOCTA-R and TACT-V programs, used by Westinghouse and General Electric, respectively, are primarily for analyses of reactor cores in loss-of-coolant accidents with the emergency core-cooling systems operating. Battelle Memorial Institute is developing a new program called ECCSA that incorporates many of the features of NURLOC to analyze this situation.^{100,198} Babcock & Wilcox^{93,99} indicate that they use a program similar to the LOCTA-R program, called SLUMP, to analyze their reactor cores in the loss-of-coolant accident situation. Combustion Engineering⁹⁴ states that they are working on a similar program.

Experiments on Core Behavior During Heatup. Experiments on core behavior, including the metal-water reaction during core heatup, are somewhat limited. As mentioned earlier, LOFT was conceived originally for the purpose of observing reactor behavior during the loss-of-coolant

accident.^{173,174} However, this program is being reoriented to study the effectiveness of emergency core-cooling systems,¹⁷⁵ and therefore studies of core behavior during the heatup phase will be limited to situations in which there is emergency core cooling. It is anticipated that the rate and extent of the metal-water reaction in this situation will be small or negligible. In support of reactor loss-of-coolant studies, LOFT has initiated an experimental program that simulates fuel-pin heatup by using mockup fuel rods heated by internal electrical resistance heaters.^{175,199} This particular program, called "Fuel Heatup Simulation Tests" or FHUST will obtain data on fuel-pin heat transfer characteristics and physical effects of the metal-water reaction up to the point where the fuel pin starts to disassemble. Atmospheres in these tests will vary from vacuum to steam, and information will be obtained about the characteristics of steam flowing through the fuel bundle.

An experiment to measure the metal-water reaction under loss-of-coolant accident conditions in a pressurized-water reactor was performed by Kubit, Stanutz, and Fultonberg.²⁰⁰ The temperatures were always less than 1000°C, and therefore there was very little metal-water reaction between Zircaloy and the surrounding steam. General Electric^{44,104} simulated the BWR core behavior in the loss-of-coolant accident by using electrically heated stainless steel mockups of their fuel rods. These tests were in connection with their emergency core spray program, and some of these simulated rods reached maximum temperatures of 2400°F (1300°C). Similar tests with Zircaloy-clad rods are being planned to investigate any possible differences that may arise because of the different cladding materials, including the effect of any metal-water reaction.²⁰¹

Analyses of LOFT Core Heatup. Many analytical programs have been used to study LOFT core heatup in a loss-of-coolant accident, since the LOFT program was originally designed for loss-of-coolant experiments. The results of these analyses are still of interest because of geometrical differences between LOFT and commercial power reactors. The results of the analyses have been reported in several references, as discussed below, but direct comparisons with core heatup in commercial power reactors are limited. The comparisons have been made with the CHEMLOC¹⁰⁷ and NURLOC programs.¹⁰⁰

It became apparent even in early simplified analyses of the LOFT core, such as those of Baker, Ivins, and Bingle^{109,178} and Jensen,^{103,179} that the rate of steam supply to the core has a major influence on the rate of fuel-pin heatup and the amount of metal-water reaction. The effect of this can be seen in Fig. 3.15, which shows the influence of the various assumptions in the NURLOC program on the central-zone midplane temperature. When the temperature reaches about 1000°C (1800°F), more rapid cladding heatup due to the metal-water reaction is observed. Also it can be seen that the cladding temperature up to that time can be described adequately by an adiabatic heatup model. As the cladding heats up further, the metal-water reaction increases and further increases the rate of cladding heatup, as shown in the unlimited steam case in Fig. 3.15. At temperatures in excess of about 1400°C (2500°F), however, the rate of reaction described by Baker and Just's parabolic relation is greater than allowable by the steam available at the reaction site. (These temperatures for the specific LOFT case shown in Fig. 3.15 are somewhat higher.) This limits the rate of the temperature increase of the fuel pin and shows that ignition of the cladding is unlikely. As mentioned in the previous section on coolant blowdown,

Fig. 3.15. Effect of Various Assumptions in the NURLOC Program on LOFT Central-Zone Midplane Temperature. (From Ref. 108)

analytical methods for predicting the coolant blowdown characteristics are not developed sufficiently to predict accurately the amount of water left in the reactor vessel. For the calculations shown in Fig. 3.15, Morrison and his associates¹⁰⁵ assumed that there was 2000 lb of water left in the reactor vessel, and the initial core temperatures were based on calculations made with the RELAPSE blowdown program.¹⁸⁹ It was assumed that this water was heated by the sensible heat from the pressure vessel's wall and by thermal radiation from the core support plate. The contribution of the latter during the first 500 sec of the accident was found to be negligible. This resulted in an exponential decrease in the steam flow rate through the core to about 8500 lb/hr at end of blowdown, 1600 lb/hr at 100 sec after rupture, and 350 lb/hr at 500 sec after rupture. A more dramatic illustration of the influence of the steam flow rate and the cladding temperature at the end of blowdown on the extent of the metal-water reaction in LOFT is shown in Fig. 3.16. These data were calculated by the CHEMLOC program,¹¹⁰ in which the initial flow rates and temperatures are specified in the input. Similar calculations with

Fig. 3.16. Effect of Cladding Initial Temperature and Steam Flow Rate on Cladding Reaction in LOFT as Calculated by the CHEMLOC Program. (From Ref. 110)

an initial temperature of 285°C and steam flow rates of 7,500 and 10,000 lb/hr show that the steam flow is sufficient to keep the core below temperatures at which the metal-water reaction would take place.

Once the steam flow rate to the reactor is known or assumed, the rate and the extent of the metal-water reaction can be calculated. The primary effect of the metal-water reaction prior to any melting of core material is to increase the rate of heatup of the fuel pins. A number of calculations have been made to determine how much the metal-water reaction affects the rate of the fuel pin heatup in LOFT. These include calculations directly connected with the LOFT program^{106,180} and those made at Battelle Memorial Institute^{105,108,197} and at Argonne National Laboratory^{109,178} for the LOFT program. Typical results of the calculations with the NURLOC program are shown in Figs. 3.15 and 3.17. It

Fig. 3.17. Temperature Histories Calculated by the NURLOC Program To Illustrate Effects of Metal-Water Reaction in LOFT Top-Break Accident with 2000 lb of Water Remaining. (From Ref. 105)

may be seen that the metal-water reaction shortens the time for the hot fuel pin at the center of the core to reach its melting temperature by about 40 sec. If unlimited steam were available for this reaction, the melting time for this pin would be reduced by about 100 sec. However, as stated earlier, the metal-water reaction is only one of the many factors that must be considered during core heatup, and this case is unrealistic. In addition to the availability of steam, these other factors include convection and radiant heat transfer, core geometry, etc. The effects of some of these other variables are also shown in Fig. 3.15.

Another interesting effect of the metal-water reaction on the LOFT core temperature during the heatup period is that the maximum temperature occurs below the core midplane. This is shown in Fig. 3.18, which gives results of the calculations for the central zone made with both the CHEMLOC and the NURLOC programs. The maximum temperature occurs below the midplane because most of the steam is consumed by the metal in the lower part of the reactor core and only hydrogen remains in the gas stream in the upper part of the reactor core. This also indicates that melting will start at some point below the core midplane as illustrated quite markedly by the CHEMLOC¹¹⁰ results shown in Fig. 3.19, in which the amounts of the core above the cladding melting temperature (1852°C) and above the fuel melting temperature (2800°C) are indicated. Figure 3.18 also shows that the results predicted by the CHEMLOC and NURLOC programs for the LOFT core are in general agreement. The minor differences arise from the treatment of gas flow, mesh spacing, etc.²⁰²

Comparisons have also been made between the results predicted by the ARC and NURLOC programs.²⁰² The difference of assuming no resistance to gaseous diffusion in calculating the metal-water reaction in the ARC program¹⁰⁶ and assuming resistance to this diffusion in the NURLOC program^{105,197,202} appears to have little effect on the fuel-pin temperature. Other factors, such as the assumptions used for the core power density, have a greater influence on the results. For relatively long periods of time, such as 20 to 30 min after the initiation of the accident, without any emergency core cooling, structural heat sinks have a great influence on core behavior.^{105,180,189,197}

Fig. 3.18. LOFT Central-Zone Temperature Profiles Calculated by the CHEMLOC and NURLOC Programs. (From Ref. 202)

It can be seen from the above discussion that many factors influence the metal-water reaction in the LOFT core during the heatup period in a loss-of-coolant accident. The predicted results depend greatly on the accident definition and other assumptions used in the calculational models. The definitions of the basic metal-water reaction rates in these cases are fairly well known in comparison with the other assumptions. Therefore future work should be concentrated more on the methods of accident definition than on the basic nature of the metal-

Percent Hydrogen in Steam
Leaving Top of Core

Temperature Profile Map (Approx.
10% of core at or above 2800°C)

Initial Core Temperature 285°C; Steam Flowrate 1000 lb/hr

Initial Core Temperature—That Corresponding to Operating Power; Steam Flowrate 1000 lb/hr

Fig. 3.19. Typical Results from CHEMLOC Computations for the LOFT Loss-of-Coolant Accident. (From Ref. 110)

water reaction. Also in accident analyses the extent of metal-water reacted in a core is often reported as the percentage of the cladding reached; however, it should be realized that this is a simplification of the actual situation since, as discussed above, many other factors have just as great or greater influence on the consequences of the accident.

Mention should be made of some simplified calculations carried out by Baker for a LOFT core with stainless steel in place of Zircaloy fuel cladding.^{9,113} These calculations were similar to the simplified calculations made earlier for the LOFT core with Zircaloy fuel cladding,^{109,178} except that it was assumed that the stainless steel did not react until it reached its melting point of about 1400°C. When the cladding temperatures rose above this value, it was assumed that the reaction rates were steam limited. Results of this calculation compared with the results for the Zircaloy-clad fuel indicate that the overall reaction for the stainless steel cladding is not so great as that for Zircaloy cladding. This is primarily due to the lower heat of reaction for the stainless steel.

Accident Analyses for Commercial Reactors. For commercial power reactors, study of the metal-water reaction is only one part of the accident analyses made to insure that the reactor containment system will not be violated. The criteria usually used in these analyses are that the fuel-pin cladding must be kept below its melting temperature¹ and that there must be negligible metal-water reaction. The analyses usually show that the amount of metal-water reaction is very limited and that there is little hydrogen produced. There is question, however, regarding the structural strength of the fuel pins after the reactor core has been cooled down by the emergency core-cooling system. There is evidence of fuel-pin failure even without melting of the cladding,⁴² and this is believed to be due to metal-water reaction taking place below the melting temperatures.⁴³ The extent to which the metal-water reaction is responsible for this is not certain. The point is that with the present knowledge it is conceivable that this type of fuel-pin failure could cause collapse of a portion of the core into a geometry such that

the emergency core-cooling system could not effectively remove heat from it. Certainly more work is urgently needed in this area.

As mentioned in the discussion of LOFT, the rate of steam flow through the core has a great influence on the extent of the metal-water reaction. Semiquantitative comparisons of the steam flow rates through the cores of LOFT, commercial PWR's, and commercial BWR's have been made by Jensen,¹⁰³ Morrison and his co-workers,¹⁰⁵ and by Hesson and Ivins.¹⁰⁷ The general consensus of these studies is that the initial boiloff rates of the water remaining in the reactor vessel normalized to the vessel's cross-sectional area are the same for all the reactors. However, the rate of dropoff of the boiloff varies with the thickness of the reactor vessel wall. This rate of decrease will be less for the commercial power reactors than for LOFT because of greater pressure vessel wall thickness. By the same token, this rate of decrease will be less for the commercial PWR's than for the commercial BWR's. Morrison and his associates¹⁰⁵ estimated that the rate of dropoff of boiloff in a 1000-Mw(e) PWR is about one-sixteenth of that in LOFT and that in a 1000-Mw(e) BWR it is about one-tenth of that in LOFT.

Analyses of PWR's by Westinghouse. In the loss-of-coolant accident analysis of their PWR's, Westinghouse calculates the amount of water left in the reactor vessel by blowdown codes such as FLASH or SATAN. As mentioned above, the amount of water predicted by these programs to be left in the vessel tends to be low. Prior to the use of the accumulator tanks in their emergency cooling system, they assumed that the amount of water left in the pressure vessel following the blowdown resulting from the double-ended failure of the largest pipe in the primary coolant system was zero. However, for smaller breaks and the use of the accumulators in all cases, there is some water in the pressure vessel at all times.²⁰³ Based on the source of heat for this boiling water being the sensible heat in the pressure vessel wall and radiation from the reactor core, they calculate the rate of core heatup by using the LOCTA-R computer program.^{36,91} With the exception of the core meltdown, which is discussed later, they assume that the metal-water reaction is described by Baker and Just's parabolic relation. Typical results of

their calculations are those for the Turkey Point reactors.^{91,98} With the use of the accumulators in the emergency cooling systems, Westinghouse calculates that there will be less than 1% metal-water reaction and that the cladding will never reach the melting temperature for any size of break in the loss-of-coolant accident.⁹⁸ If the contents of only one of the three accumulator tanks reached the core, there would be about 5% metal-water reaction resulting from the double-ended failure of the large primary coolant piping. No accumulator action would result in about 14% metal-water reaction. Estimates of the rate of metal-water reaction and the cladding hot-spot temperature for this situation are shown in Figs. 3.20 and 3.21. It can be seen that there is less than 1% metal-water reaction and the cladding hot-spot temperature just reaches the melting temperature in about 50 sec after the break. The rate of the metal-water reaction increases rapidly after this time, since much of the core is presumably above 1000°C. This is the temperature at which Westinghouse assumes that the metal-water reaction starts.

Fig. 3.20. Metal-Water Reaction in Turkey Point Reactor Loss-of-Coolant Accident with Partial Safety Features and No Accumulators. (From Ref. 97)

Fig. 3.21. Cladding Hot-Spot Temperature in Turkey Point Reactor Loss-of-Coolant Accident with Partial Safety Features and No Accumulators. (From Ref. 97)

The sensitivity of the core thermal transient in a loss-of-coolant accident to a number of input parameters in their analytical programs has been reported by Westinghouse for the Diablo Canyon PWR,¹¹² which is a very recent design. They found that using the energy from the metal-water reaction to heat up the steam to the reaction temperature reduced the cladding peak temperature only from 2121 to 2110°F. Changing the activation energy constant in Baker and Just's relation for the metal-water reaction energy had a considerable influence on the peak cladding temperature, as can be seen in Table 3.8; but changing the diffusion constant in this relation did not. This was to be expected, since the activation energy is in the exponential part of this relation and the diffusion constant is in the linear part. The effects of the cladding emissivity and accumulator water temperature are little, but the effect of the heat transfer coefficient is significant.

Table 3.8. Effect of Varying the Constants in Baker and Just's Relation for the Metal-Water Reaction on the Peak Cladding Temperature for a Loss-of-Coolant Accident in the Diablo Canyon PWR^a

Activation Energy	Diffusion Constant	Peak Cladding Temperature (°F)
Baker's nominal value	Baker's nominal value	2121 (design)
Nominal value increased 10%	Nominal value	2070
Nominal value decreased 10%	Nominal value	2336
Nominal value	Nominal value increased 20%	2142
Nominal value	Nominal value decreased 20%	2100

^aFrom Ref. 112.

Analyses of PWR's by Babcock & Wilcox. The approach that Babcock & Wilcox^{93,99} use in analyses of the loss-of-coolant accident is quite similar to that of Westinghouse. For the analyses of the consequences of all sizes of breaks in their PWR primary cooling system, including the double-ended failure of the largest pipe, they assume that the coolant blowdown is described by a modified version of the FLASH program. They calculate the amount of water left in the vessel at all times by taking into account the effect of the accumulator tanks in the emergency core-cooling system. Core heatup is described by another computer program called SLUMP, which is similar to the programs described in Tables 3.6 and 3.7 (Ref. 99). As in the other programs, the metal-water reaction is described by Baker and Just's parabolic relation. With the accumulators and the minimum of other engineered safety features, Babcock & Wilcox⁹⁹ calculate for the Oconee reactor that less than 0.005% metal-water reaction would take place in the core and that the temperatures of all the cladding would remain below the melting temperature. Prior to incorporating accumulator tanks in the Oconee reactor, Babcock & Wilcox calculated the extent of metal-water reaction and the extent of core meltdown as a function of the emergency

core-cooling system injection flow rate.⁹³ The model was somewhat simplified compared with the one described above, but it followed the same general approach. No water was assumed to be left in the pressure vessel at the end of blowdown, and the cladding was assumed to melt at 3375°F (1850°C). When the molten cladding dropped into the water at the bottom of the pressure vessel, 10% additional metal-water reaction was assumed. Results of these calculations are shown in Fig. 3.22 for

Fig. 3.22. Reacted and Melted Cladding as a Function of the Emergency Core-Cooling System Injection Flow Rate Without Accumulators Following a 36-in.-Pipe Rupture in the Oconee Reactor. (From Ref. 93)

emergency cooling system operation delay times of 16 and 38 sec, which are the starting times for normal and emergency power, respectively. The normal injection flow rate is 14,000 gpm and the minimum is 8,000 gpm. In the worst case, the amount of metal-water reaction and cladding melting would be less than 1%.

Analyses of PWR's by Combustion Engineering. In the case of Combustion Engineering, methods of predicting the consequences of a loss-of-coolant accident are still under development.^{94,204} However, they too have added accumulator tanks to their emergency core-cooling system design to prevent cladding melting and limit the amount of metal-water reaction. Prior to inclusion of these tanks, they calculated the extent of the metal-water reaction and cladding melting for the double-ended failure of the largest pipe in the system based on adiabatic heating of the fuel pins and Baker and Just's parabolic relation for the metal-water reaction rate. For this model, they reported that 84% of the cladding would melt before the core was flooded with water from the emergency core-cooling system. The amount of cladding reacted was 23%; 18% reacted in the core and another 5% reacted when it melted and dropped in the water below the core. It should be remembered that these particular results are based on some very preliminary calculations.

General Conclusions Relative to PWR's. In summary, the importance of the rapid action of the emergency core-cooling system to limit the extent of the metal-water reaction is to be emphasized. Any delay in the action of such a system would result in a considerable increase in the extent of the metal-water reaction and melting of the cladding. This is discussed to a much fuller extent in Lawson's report on emergency core-cooling systems.² The safety analysis reports do not give much detail on the temperature distribution within the core during the loss-of-coolant accident. However, calculations have been made by Hesson and Ivins¹⁰⁷ for a PWR typical of the size being built at the present time. In comparing this reactor with the LOFT reactor they noted, as is shown in Table 3.3, that the power densities in the two reactors are about the same, although LOFT of course has a much lower overall power. The cores in the PWR and LOFT heated up at about the

same rate, which indicated that the heatup rates are not very dependent on the reactor power. However, the extent of the metal-water reaction was much less in the large PWR. This is because the fuel pins in this reactor are much longer, 12 ft versus 3 ft for LOFT, and the amount of steam entering the reactor core per unit cross-sectional area is about the same for both reactors. Most of the steam is consumed in the lower part of the PWR core, and the metal in the upper part of the core is denied the steam necessary for the metal-water reaction. Thus the importance of the length of the fuel pins on the extent of the metal-water reaction is demonstrated.

Analyses of BWR's by General Electric. General Electric considers the entire spectrum of pipe breaks in their analyses of the BWR loss-of-coolant accident.^{37,96} The worst case is the double-ended failure of the main coolant recirculation line. Coolant blowdown is calculated by their RIP program, and it is assumed that the vessel is drained dry prior to the action of the emergency core-cooling system. Core heatup is described by the TACT-V computer program, for which it is assumed that the metal-water reaction can be described by Baker and Just's parabolic relation. Typical results are shown in Fig. 3.23, which indicates that 0.6% of the cladding and fuel-element channel material reacts with the steam and none of the cladding melts. General Electric reported a sensitivity study on their method of core heatup analysis for the Oyster Creek BWR.¹¹¹ They considered the effect of heating the steam at the local metal-water reaction site by the heat of reaction and the effect of the amount of steam being supplied to the cladding. For the base case it was assumed that the steam was brought up to reaction temperature by the local metal-water reaction and that there was 100% steam availability. Assuming that the steam was at the reaction temperature had little effect on the peak cladding temperature if the emergency core-cooling system was operating, but it shortened the time to reach cladding melting from 211 to 173 sec if there was no emergency core cooling. Limiting the availability of steam to 50% again had little effect on the peak cladding temperature if the emergency core-cooling system was operating, but it lengthened the time to reach cladding melting from 211 to 256 sec. The peak cladding temperature with

Fig. 3.23. Metal-Water Reaction and Cladding Temperatures in a Loss-of-Coolant Accident for the Browns Ferry BWR. (From Ref. 37)

emergency core cooling was also found to be somewhat sensitive to the blowdown dryout time but insensitive to the radiation emissivity and the core spray temperature.

As for the PWR's, the General Electric calculations demonstrate the importance of the rapid action of the emergency core-cooling system to limit the core temperatures and the metal-water reaction. A delay in the action of such a system would result in a considerable increase in the extent of the metal-water reaction in the BWR's too. Additional core heatup calculations for BWR's similar to the Browns Ferry reactor have been made by Hesson and Ivins¹⁰⁷ with the CHEMLOC program and by Morrison and his associates¹⁰⁰ with the NURLOC program. Both showed the more rapid heatup of the lower part of the core region due to the metal-water reaction, as illustrated in Fig. 3.24. The steam entering each radial region of the core is consumed by the metal in the lower part of the core, and little or no steam is available for the upper part of the core. As for PWR's the long length of the BWR fuel pins makes this effect more noticeable than for reactors with short fuel pins, such as LOFT. Power densities are lower in BWR's than in PWR's

Fig. 3.24. Axial Temperature Distributions in the Maximum Radial Power Zone of a 1000-Mw(e) BWR as Calculated by NURLOC. (From Ref. 100)

and LOFT, and this results in slower core heatup times and slower metal-water reaction rates. Because of this the metal-water reaction contributes less to the core heatup in BWR's than in PWR's and LOFT. Also the power density distribution in the core is important, as can be seen by comparing the core heatup in LOFT shown in Fig. 3.18 with that for the BWR shown in Fig. 3.24.

The core temperatures predicted by the TACT-V, CHEMLOC, and NURLOC programs for the Browns Ferry BWR were compared.²⁰⁵ For these particular calculations, the state of the reactor core and the amount of water left in the pressure vessel at the end of blowdown were assumed to be identical. The core temperatures predicted by the three programs agreed remarkably well for the first 80 sec after the start of the

accident. After that time, the temperatures predicted by the TACT-V program rose at a faster rate because of the assumption of unlimited steam available for the metal-water reaction. However, the agreement between the CHEMLOC and the NURLOC programs for these later times was very good.

In the light of the present experimental information, the various reactor core heatup programs are sufficiently sophisticated to predict the fuel-pin temperatures and to show that the metal-water reaction should be treated as only one part of an integral model of the core. The particular items greatly influencing the rate and the extent of metal-water reaction are the magnitude and the distribution of the core power density, the temperature distribution at the end of blowdown, steam supply to the core, the length of fuel pin, core region heat transfer coefficients, and the time for the emergency core-cooling system to act. Reactor power levels and the nature of the diffusion of steam through the hydrogen-rich film adjacent to the fuel pins appear to have little effect on the metal-water reaction. Also the emissivity of the cladding appears to have little influence on the fuel-pin temperature history. Therefore heat transfer from the fuel pins should not be altered much as the cladding becomes oxidized by the steam. Unless the rate of metal-water reaction is limited by the steam flow rate, it is assumed for these programs that the reaction is described by Baker and Just's parabolic relation. Any variation in the activation energy has a great influence on the fuel-pin temperature, since this constant is an exponential term in this relation. Thus the relation recently reported by White¹⁷ suggests that the use of Baker and Just's relation is conservative. The effect of varying the linear diffusion constant in these relations on the fuel-pin temperature history is small.

Limitations of Criteria of No Cladding Melting and Negligible Metal-Water Reaction. All the reactor manufacturers use these heatup programs to demonstrate that the emergency core-cooling systems will prevent cladding melting and limit or prevent any metal-water reaction in the event of a loss-of-coolant accident. The criterion of negligible metal-water reaction is difficult to interpret quantitatively because of the recent data from ANL,⁴² with which it has been shown that there

can be fuel-pin collapse even if the cladding does not reach its melting temperature. This is now believed to be due to the metal-water reaction,⁴³ and more work is necessary to determine how much metal-water reaction is required to cause this. It is recommended that this work be undertaken at once, since it is assumed for all the computer programs that the fuel pins remain in their original geometry. Also high fission-gas pressure and low tensile strength of Zircaloy at high temperatures may result in cladding failure. Recent experiments and calculations indicate that the breaks in the cladding will be relatively small and that there will be no gross movement of the UO₂ fuel. It is recognized that this cladding swelling and failure due to the high pressures and the cladding fragmentation are not independent of each other in a given reactor accident. More work is needed here also. The effect of all this on the effectiveness of the emergency core-cooling system is beyond the scope of this report, and the reader is referred to the report by Lawson² for a discussion on this subject.

3.3.6 Core Meltdown and Associated Metal-Water Reaction

The above discussion of the metal-water reaction during core heatup is directed primarily to the situation in which the core is cooled immediately by the emergency core-cooling system. For this situation the core was assumed to retain its general form, and the amount of metal-water reaction was limited or negligible. If for some very unlikely reason there was no action by the emergency core-cooling system, the reactor core would eventually melt. The mode and the nature of the core melting process is subject to much speculation and conjecture. Since the rate and extent of the metal-water reaction are dependent on the core geometry, many assumptions have been made about the meltdown process to get an idea about the extent of the metal-water reaction for this situation. As pointed out by the special task force headed by Ergen in a report on their study of reactor accidents involving core meltdown,¹ the various parameters should be considered in the framework of the entire accident rather than by themselves. After studying this situation, they recommended that the best defense against core meltdown

is the use of the emergency core-cooling systems. They considered methods of handling large molten masses, such as water-cooled crucibles, large sandpiles, and holes in the ground. The effectiveness of these systems cannot be proved or disproved, and they should be studied further in a small well-designed research program. The task force also pointed out that this is a complex problem and that the extent of the research on this subject should be weighed against the potential value to be gained from it.

It is beyond the scope of this report to enter into a discussion of all facets of the complex problem of core meltdown, and therefore only the portions of this problem relating to the metal-water reaction are discussed. It is generally agreed¹ that following the double-ended failure of the largest pipe, portions of the core would reach 1850°C, the melting temperature of Zircaloy, in about 50 to 100 sec. The metal-water reaction would contribute to the heatup process and might alter the melting point of the cladding due to the formation of the oxide on the surface. However, the core would eventually melt and fall to the bottom of the pressure vessel, where there would be significant accumulation of core debris in about 10 to 60 min after the start of the accident. The extent of metal-water reaction during this period would depend on the mode of meltdown and the availability of water and steam. In another 20 to 60 min, this debris probably would have melted through the pressure vessel and passed into the containment vessel, where additional metal-water reaction could take place. Steam explosions could possibly occur during this melting process that could break up the metal and provide more surface area for the metal-water reaction. Also shock waves, such as have been observed in the steel and aluminum industry, could occur.^{62,114} The "flat-top" transient experiments of TREAT did not produce any pressure pulses upon the meltdown of the fuel-pin samples into the pool of water.^{48,137} However, steam explosions are very complicated,^{1,43} and more research is needed in this field. One other problem connected with this very degenerate case of a molten core is the long-term generation of hydrogen by the metal-water reaction.¹ Although the melted core probably would be very dense and therefore a minimum area would be available for the metal-

water reaction, long-term metal-water reaction could generate sufficient hydrogen to create excessive pressures in the containment vessel.

As mentioned earlier, calculational models based on many assumptions have been used to gain some idea of the extent of the metal-water reaction for this situation. For example, Westinghouse^{91,97} calculated 29.3% metal-water reaction for the Turkey Point reactor by using one of these simplified models. The core was divided into five annular rings, and heat balances were written for each ring based on the parabolic reaction-rate relation for the metal-water reaction. The time for each of these rings to reach its melting point (assumed to be that of ZrO_2 at $2700^\circ C$) was calculated. It was assumed that the water level in the vessel after blowdown was just below the core, and then the rate of water boiloff was calculated by using sensible energy from the slumped core, radiation energy from the portion of the core remaining in place, and sensible energy from the pressure vessel wall. The steam-limited metal-water reaction rates were then determined from this boiloff rate. It was estimated that three of the annular rings would melt in 125, 200, and 300 sec and that the molten material would melt through the vessel in 42 min. The extent of the metal-water reaction found at various times by using this model is shown in Fig. 3.25.

General Electric¹⁶⁶ uses the TACT-V program to calculate the metal-water reaction for the meltdown situation. Results of their calculations are shown in Fig. 3.26, which shows that the cladding temperatures increase very rapidly just prior to meltdown. This occurs because the metal-water reaction is described in this program by Baker and Just's parabolic relation, and the availability of the steam is not questioned. The extent of metal-water reaction for the Browns Ferry BWR based on General Electric's model is 26.5%, of which 23.5% is due to the reaction within the reactor core prior to the melting of the cladding. The melting point was assumed to be that of Zircaloy ($1850^\circ C$). The other 3% reaction was assumed to be due to reaction of melted metal in the water below the core. This is based on some of General Electric's experiments which show that the Zircaloy would melt and form about 3/8-in.-diam droplets. These molten metal droplets

Fig. 3.25. Metal-Water Reaction in Turkey Point Reactor Loss-of-Coolant Accident with No Emergency Core Cooling. (From Ref. 97)

would then fall into the water and form a 60- μ layer of oxide on its surface, which is equivalent to the 3% reaction. The 60- μ value is based on the results of Baker's condenser discharge work.⁴¹ If the cladding remained in place until the ZrO_2 melting point was reached, General Electric¹⁶⁶ estimates by using their model that there would be 60% metal-water reaction. Figure 3.26 shows that the core starts to melt in about 100 sec and that 50% of the cladding is melted in about 600 sec.

Similar calculations were made by Jensen in predicting the consequences of the meltdown of the LOFT core.^{103,179} He arbitrarily divided the core into 25 annular rings and assumed adiabatic heatup of the fuel pins in these rings. Heat sources are the decay heat and the metal-water reaction heat, with the rate of the metal-water reaction being limited either by the parabolic reaction rate relation or the availability of steam. It was further assumed that each radial ring

Fig. 3.26. Cladding Temperatures and Metal-Water Reaction in Browns Ferry Reactor Loss-of-Coolant Accident with No Emergency Cooling. (From Ref. 166)

of the core fell into the water and remained in the pressure vessel when the temperature of that portion of the stainless steel restraining grid reached its melting point ($\sim 1400^{\circ}\text{C}$). An additional 10 to 15% reaction of the unreacted material took place during the quenching of the fallen core material. These calculations indicated that the central part of the core would drop into the water about 12 min after the start of the accident and that the outer ring would drop into the water about 23 min after the start of the accident. Another simplified calculation¹⁷⁹ that took into account the thermal radiation effects indicated that the cladding would start to melt in about 325 sec and all of it would melt in about 1 hr. No attempt was made to separate the effects of the metal-water reaction from those of the decay heat on the meltdown times, and thus all that can be said is that the metal-water reaction does contribute to the heatup process and shortens the time required to reach the cladding's melting point.

Both the NURLOC^{100,105,197} and CHEMLOC¹⁰⁷ core heatup programs analyze the metal-water reaction in the core during meltdown. The meltdown models being used in these programs are more sophisticated than those described above, but they are still quite arbitrary. They are, of course, more elaborate programs that take into account items such as radiative heat sinks, including the control rods, and other structural material within the core. In the NURLOC program^{105,197} the meltdown process consists of homogenizing the fuel-pin material, letting it fall to the first pin spacer below the location of the melting, letting it melt through that spacer and fall to the next one, and so on until it falls to the restraining grid. It then is allowed to melt through this grid and fall to the support plate, melt through it, and fall to the bottom of the pressure vessel. Steam flow through each radial channel is assumed to stop at the point of melting. The CHEMLOC program¹⁰⁷ uses somewhat a similar approach, but factors are added for the amount of core material bridging between the fuel rods, the amount dripping to the bottom of the reactor core, and the amount falling out of the reactor core. Steam flow in this model is assumed to be stopped when a predetermined number of rods in each region have slumped.

Amounts of metal-water reaction in the cores of LOFT and a 1000-Mw(e) BWR calculated by the NURLOC program are shown in Fig. 3.27. The cores were broken up into ten annular rings for these computations, and

Fig. 3.27. Percentage of Zircaloy Cladding Reacted as Calculated by the NURLOC Program. (From Ref. 100)

it can be seen that the channel blockages occur sooner for LOFT than for the BWR. First channel blockage occurred at 170 sec in LOFT and 380 sec in the BWR, and the ninth channel blockage occurred at 360 sec in LOFT and at 640 sec in the BWR. These differences are due to the higher power density in LOFT and the longer fuel rods in the 1000-Mw(e) BWR. In the linear portion of these curves, it was determined that the metal-water reaction heat is about equal to the decay heat in LOFT, and it was about 25% of the decay heat in the BWR.¹⁰⁰ Comparing the results shown in Fig. 3.27 with those of General Electric for the Browns Ferry reactor¹⁶⁶ shows much less metal-water reaction based on the NURLOC program. Much of this of course is due to General Electric's assumption of unlimited steam supply and the NURLOC assumptions of limited steam supply and no steam flow upon core slumping within the channel. Another interesting point in the NURLOC computations for LOFT was the effect of the control rods as sinks for the temperature rise.¹⁰⁰ They found that after meltdown in the central core region the rate of temperature rise in that region was about twice as high when not considering these rods as when considering them.

The CHEMLOC program also predicted much longer times before core meltdown in the 1000-Mw(e) BWR.¹⁰⁷ At 3200 sec after the initiation of the accident, this program predicted 26% metal-water reaction in LOFT, 16% metal-water reaction for the cladding in a 2758-Mw(th) PWR, and 14% metal-water reaction for the cladding and 6% metal-water reaction for the fuel element channel in a 2255-Mw(th) BWR. Most of the 26% metal-water reaction for LOFT took place within the first 1200 sec of the accident. This reflected the effect of the shorter fuel pins and the higher power density in LOFT. The rate of the metal-water reaction and core heatup in the PWR would be slightly greater than that in the BWR due to the difference in the power density. However, the rates of the metal-water reaction in these two reactors are not greatly different after the first 800 sec of the accident, since it is governed by the rate of steam flow available to the core, which is not greatly different for the two reactors. Of course the rate of temperature increase in the PWR core is still greater because of its higher power density.

The amount of metal-water reaction in the reactor core without any action by the emergency core-cooling system is lower as calculated by the NURLOC and CHEMLOC programs than it is as calculated by the simplified models of General Electric and Westinghouse. This indicates the strong effect of the core geometry before, during, and after meltdown on the rate of the metal-water reaction. Also the availability of the steam or water to the metal is very important when the metal temperatures are higher, say above 1200 or 1300°C. To get a better estimate of the metal-water reaction during the meltdown period, experiments are needed to understand the fuel-rod melting and collapse process, the modes of the core redistribution, failure of the core support plate and pressure vessel, etc.¹ However, this is a very complex process, and extensive experimentation would be required to understand it fully. Therefore, as mentioned earlier, the potential benefits to be gained from these experiments should be weighed against the amount of experimentation that would be required.¹ On the basis of present knowledge, the extent of the metal-water reaction up to the time at which the core has melted down is estimated to be in the range 25 to 50%.

3.3.7 Fate of the Hydrogen Produced by the Metal-Water Reaction

Hydrogen is produced by the metal-water reaction in the reactor core region, and this must be considered in the analysis of a loss-of-coolant accident. Although it is recognized that there possibly could be absorption of hydrogen in Zircaloy at high temperatures, as discussed in the previous chapter, it is commonly assumed that the hydrogen passes out of the core and into the containment vessel through the primary coolant system break. This hydrogen is then assumed to burn in the analyses of the containment vessels for the PWR's and not to burn in the analyses of the containment vessels for the BWR's. In these analyses, the reactor manufacturers show that the containment vessels can accommodate the various energy sources generated in the loss-of-coolant accident. It is beyond the scope of this review to evaluate these analyses, and therefore this discussion is limited to some of the problems associated with the hydrogen-air reaction.

The first problem is to know the rate of hydrogen generation, which is dependent on the definition of the accident.^{80,103} As pointed out by Moore and Gilby,⁸⁰ the assumption that all the steam passing through the core reacts with the metal is not necessarily the pessimistic one if the hydrogen-air reaction is considered. This is because of the possibility of small amounts of hydrogen forming and passing out into the containment vessel unreacted. This hydrogen could pocket within the vessel and form a potential for an explosion or a detonation. The two most elaborate programs that analyze the hydrogen generation in a loss-of-coolant accident are the NURLOC and CHEMLOC core heatup programs. Results of using these programs to predict the hydrogen concentrations in the central region of the LOFT core are shown in Fig. 3.28. They show that before about the first 240 sec has elapsed after the accident, not all steam passing through the core reacts with

Fig. 3.28. Hydrogen Concentration Profiles for LOFT Central-Core Zone as Calculated by the NURLOC and CHEMLOC Programs. (From Ref. 202)

the metal. However, after this time, it does, and Morrison and his co-workers¹⁰⁵ estimate that the hydrogen concentration in the gas leaving the LOFT core could be as high as 48%. The differences in the hydrogen concentration profiles as calculated by the two programs are due to the assumptions regarding the variation of the gas velocity through the reactor core. Hesson and Ivins¹⁰⁷ calculated the hydrogen concentration in the gas leaving the core of a typical commercial PWR and a typical commercial BWR. The time when all the steam passing through the core reacts with the cladding is lower for the PWR (300 sec for the PWR versus 1100 sec for the BWR) because of the higher power densities in the PWR.

Another possible source of hydrogen in a loss-of-coolant accident is the radiolytic decomposition of the water used in the emergency core-cooling system. Both Westinghouse³⁶ and General Electric²⁰⁶ have investigated this situation. Based on the work of Jenks,⁸² Westinghouse calculated that the hydrogen concentration distributed uniformly in the containment vessel would be less than 3.3 vol % for the coolant boiling around the core for one week. If the coolant were not boiling, the uniform hydrogen concentration in the containment vessel would be 2.53 vol %, which is below the hydrogen flammable limit. The latter value is lower than the former value because of Henry's law for hydrogen dissolved in the water, which is in equilibrium with the hydrogen in the gas phase, and thus forces some recombination of the hydrogen and the oxygen. General Electric calculated from the work of Breden⁸³ that the hydrogen concentration in the drywell is less than 3.2 vol % when the core has been submerged in the coolant water for 1000 hr (~6 weeks). This is again below the hydrogen flammable limit. In the case where the core is surrounded by steam, the amount of radiolytic hydrogen produced will be negligible compared with the hydrogen produced from the metal-water reaction.

The main uncertainty in all these calculations is the possible pocketing of the hydrogen within the containment vessel, since this would give rise to mixtures that could possibly explode or detonate. The uncertainties regarding the explosion and detonation limits of

hydrogen-air mixtures are covered in the previous chapter, and therefore they are not reported here. An explosion of a hydrogen-air mixture apparently did occur in the EBR-II transfer air lock.⁴³ In this case a battery on the transfer cask was overcharged and produced hydrogen, which is thought to have accumulated in the upper part of the air lock. Preliminary calculations by Hesson and Ivins⁴³ indicated that the buoyant nature of the hydrogen overcame the mixing effects, such as diffusion and convection, and allowed the hydrogen to pocket.

In the analysis of the containment vessels for the PWR's, it is assumed that the hydrogen produced by the metal-water reaction burns as it leaves the primary coolant system or shortly afterwards. This implies that the hydrogen is above its spontaneous ignition temperature and in a concentration that allows burning (see Fig. 2.31). However, there are many uncertainties regarding the spontaneous ignition temperatures, as discussed in the previous chapter, and there is no assurance that in every loss-of-coolant accident the hydrogen will leave the primary cooling system at above its flammable limit. In this situation it is conceivable that the buoyant nature of the hydrogen can overcome the tendency to mix by diffusion and natural and forced convection, and the hydrogen can pocket in the containment vessel. This could occur also for the case where there is radiolytic decomposition of the water, as discussed above.

Another item pointed out by Jensen¹⁰³ is that hydrogen often burns with a diffusion type of flame when it is above its spontaneous ignition temperature. The length of this flame is proportional to the flow rate of the hydrogen leaving the primary cooling system and inversely proportional to the diffusivity of hydrogen in air. Jensen indicated that the length of this flame could be as much as 20 ft in the large power reactors. The consequences of the direct impingement of this flame on the surrounding structures could be very serious.

These uncertainties, along with those described in the previous chapter, indicate the need of additional experimental information regarding the possible explosive hazard of hydrogen within reactor containment vessels. These should include buoyancy of hydrogen in hydrogen-air

mixtures versus the mixing of hydrogen in such mixtures by diffusion and natural or forced convection, and further studies should be made of the detonation limits, including the effect of diluents and vessel size and geometry.

It has been suggested often that one way to eliminate the hydrogen-air problem in containment vessels is to provide an inert vessel atmosphere by filling it with nitrogen. In general, reactor manufacturers are currently strongly opposed to this. Entrance to the containment vessel during reactor operation is required to do normal maintenance and inspection on various reactor components, and an inert atmosphere in the containment vessel would make this very difficult. The vendors argue that a less-safe overall situation would result because the inspection and maintenance would be less frequent than with air in the containment vessel.

General Electric is making provisions to provide inert atmospheres in the drywells of their BWR's, but they are very much opposed to activating them. Their position was stated as follows at the public hearing for the Vermont Yankee reactor:¹¹⁶

MR. BRIGGS: I had another short question here concerning containments. I believe in the language of the reports it says that provision will be made for inerting the containment. The question is will the containment be inerted or will it not be inerted.

MR. BRAY: Simply stated, all necessary inerting equipment shall be provided. It is our hope that prior to the operating license time we can, through presentations of detailed behavior characteristics, demonstrate to the full confidence of the Staff that the activation of such equipment may not be required. But we are providing the full containment atmospheric control system.

4. CONCLUSIONS

4.1 General Role of Metal-Water and Hydrogen-Air Reactions in Reactor Accidents

The metal-water reaction is only one of the many factors that must be considered in a hypothetical reactor accident, and these factors are not necessarily independent. For example, the rate of the metal-water reaction is strongly dependent on the temperature of the metal and the availability of the steam to the metal surface. Factors such as the core geometry, the reactor power density and distribution, and the nature of the fuel-pin failure, if any, influence the course of the accident. Since the metal-water reaction is a source of hydrogen in a reactor accident, the factors affecting the rate of metal-water reaction also affect the nature of the possible hydrogen-air reaction. Therefore accident definition is a very important factor in determining the extent of the chemical reactions. Only by performing an integral analysis of a reactor accident can the true rate and extent of the metal-water reaction be ascertained. Simplified analyses that separate the effect of the metal-water reaction are sometimes used in containment vessel design, but it should be remembered that the amount of chemical reaction predicted in these analyses is at best a crude estimate.

4.2 Basic Rate Relations for the Metal-Water Reaction

The metal-water reaction in hypothetical reactor accidents is limited by the temperature of the metal or by the availability of steam or water to the metal surface. Much of the experimental effort has been directed toward the determination of the reaction rates between zirconium and its alloys with steam, since it is used almost universally as a cladding material in light-water power reactors. The relation commonly used to predict the temperature-limited metal-water reaction for this material is that developed by Baker and Just.⁴¹ White¹⁷ suggested a slightly modified version of this relation, but the difference between the rates predicted by his and Baker and Just's relation

is small. Both these relations indicate parabolic reaction rates and that there is no significant reaction until the metal temperature is at least 1000°C . They were developed for the rate of oxygen uptake in the zirconium, since all the reaction product is not ZrO_2 (unless the metal is completely oxidized). The various accident analyses are based on the assumption that the reaction product is ZrO_2 , but the error introduced by this assumption is small compared with the errors of the other assumptions used in these analyses. If the hot zirconium is in air, the rate of weight gain of the metal is greater than in a steam atmosphere, since it reacts with the nitrogen in addition to the oxygen in the air.

Although stainless steel is no longer much used as a cladding material for light-water power reactors, much work has been done in determining the reaction rates between this material and steam. The basic mechanism of the reaction of stainless steel with steam is not quite clear because stainless steel tends to froth near its melting point ($\sim 1400^{\circ}\text{C}$). Below its melting point, the reaction rate after the initial period of a few minutes appears to be parabolic,¹⁷ and it becomes significant for temperatures above 1200°C . A good approach for analyzing the rate of the stainless steel-steam reaction in a reactor accident is to assume no reaction until the melting point of the stainless steel is reached and then steam-limited reaction until the metal is consumed. Compared with the other assumptions made in accident analyses, the error introduced by this assumption is small.

The presence of any hydrogen in the steam adjacent to the UO_2 fuel will greatly retard the UO_2 -steam reaction because of the law of mass action. Steam reacting with the cladding in the reactor core generates sufficient hydrogen to cause this retardation. Therefore unless all the cladding has reacted, the UO_2 -steam reaction can be ignored.

4.3 Metal-Water Reaction in Nuclear-Excursion Accidents

The role of the metal-water reaction in nuclear-excursion accidents appears to be minor. TREAT experiments indicate that there is little metal-water reaction until the fuel starts to melt, and it increases linearly with the fission energy input to the fuel. However, the main

concern of a nuclear-excursion accident is damage to the primary cooling system (or any additional damage in case of a rod-ejection accident) and to the core such that the core cannot be cooled after the excursion. Some preliminary analyses have shown that energies required for damaging the primary cooling system result in serious damage of the core.

The general approach so far in power-reactor safety analyses is to show that the fuel pins do not fragment during the nuclear excursion. This preserves the original heat transfer area and therefore limits the pressure pulse that can be generated. The TREAT data show that fragmentation of the fuel pins does not occur until most or all the fuel is molten, which is equivalent to a peak enthalpy of 280 cal/g UO_2 . Excursions resulting in fission energy inputs to the fuel greater than 280 cal/g UO_2 but less than 360 cal/g UO_2 , where the UO_2 vapor pressure is 1 atm, have been suggested recently as safe upper limits. The fuel could then fragment and create an increased surface area for transfer of fission energy from the fuel to the water, which could cause a more severe pressure pulse. The questions then are how this fission energy input is converted into mechanical energy and how this mechanical energy is dissipated in the reactor system? Additional metal-water reaction occurs in this situation, but it is small compared with the fission energy associated with the nuclear excursion. Also the rate constants associated with the metal-water reaction are low compared with those for the transfer of heat from the fragmented fuel to the coolant water.

4.4 Metal-Water Reaction in Loss-of-Coolant Accidents

The extent of metal-water reaction in a loss-of-coolant accident depends on the effectiveness of the emergency core-cooling system. (The reader is referred to the review report by Lawson² for further information on this subject.) The present criteria states that the emergency core-cooling system will prevent any melting of the cladding and will limit the extent of the metal-water reaction to negligible values; however, if for some very unlikely reason the emergency core-cooling systems failed to operate properly, the extent of the metal-water reaction could be significant and the cladding could melt.

There is some question about interpreting the criterion that the emergency core-cooling system limit the extent of the metal-water reaction to a negligible amount. In some simulation experiments with core spray systems, Wilson⁴² found that the fuel pin would fragment even if the cladding did not reach its melting temperature. It is conceivable that this could result in the collapse of a sufficient amount of the reactor core that it could not be cooled effectively by the emergency core-cooling system. It is believed that this fragmentation is due to the metal-water reaction that takes place,⁴³ although it is recognized that the temperature-time history of the fuel pin and the oxidation of the cladding are not independent of each other. The extent of metal-water reaction required to cause this brittleness of the Zircaloy cladding is not certain.

The state of the reactor at the end of the blowdown phase of a loss-of-coolant accident influences greatly the rate and extent of metal-water reaction that may take place. Experimental data for the transient heat transfer coefficients during the blowdown phase are limited. These influence the fuel-pin temperatures at the end of blowdown noticeably, and these temperatures affect the fuel-pin temperature excursion history and the rate of metal-water reaction. The amount of water left in the pressure vessel at the end of blowdown is very important, since this is the primary source of steam for the metal-water reaction. Many analyses show that the rate of the metal-water reaction in a loss-of-coolant accident is limited by the rate of steam flow in the core. Methods for predicting the blowdown characteristics of a reactor have not been developed sufficiently well to predict accurately the amount of water left in the pressure vessel; the amount predicted tends to be too low. Heat for boiling this water is the sensible heat in the wall of the pressure vessel, and therefore the steam formation rate and metal-water reaction are dependent on the pressure vessel wall thickness. Radiant heat from the core to this pool of water appears to have little influence on the steam-generation rate.

Computer programs describing the heatup characteristics of reactor cores, such as NURLOC and CHEMLOC, are sufficiently sophisticated in the light of the present experimental data. Reactor power density and

the length of the fuel rods have an important bearing on the rate of metal-water reaction during a loss-of-coolant accident. Higher power densities and shorter fuel rods lead to greater metal-water reaction. Local power densities affect the local fuel rod heatup characteristics and local metal-water reaction, but they have little influence on the extent of the overall metal-water reaction in the reactor core. The percentage metal-water reaction in a reactor core is not sensitive to the reactor power level, the rate of diffusion of steam through the hydrogen-rich film adjacent to the cladding, or the emissivity of the cladding surface. The latter implies that oxidation of the rod surface affects the temperature history of the fuel rod very little. However, variations in the value of the heat transfer coefficient of the steam flowing through the core will influence the nature of the temperature excursion and therefore the metal-water reaction. Any variation in the exponential activation energy in the parabolic relation for metal-water reaction would influence the extent of the metal-water reaction in the core very much, but any variation in the linear diffusion constant in this relation would have little effect.

The computer programs describing the core heatup are based on the fuel pins remaining in their original geometry during the heating process (except when the cladding starts to melt). There will be some swelling and bursting of the cladding during this process due to the high fission-product gas pressure within the fuel pins and the relatively low tensile strength of the Zircaloy cladding at the higher temperatures. Experiments simulating this situation so far indicate that the bursting of the fuel pins occurs as localized longitudinal cracks in the cladding and does not result in gross migration of the UO_2 fuel. The effect of the swelling of the cladding during this period on the effectiveness of the emergency core-cooling systems is beyond the scope of this report and is discussed by Lawson.² However, it appears that it would have little influence on the extent of the metal-water reaction that may take place; unless of course the swelling of the cladding interferes with the steam flow or with cooling water flow through the core. This and the question of the possible core fragmentation

even without cladding melting, as described earlier, suggest that the assumption of original pin geometry should be further examined.

4.5 Core Meltdown

It is difficult to predict the extent of the metal-water reaction during the meltdown of a reactor core since not much is known about the meltdown process. However, preliminary analyses indicate that 25 to 50% of the cladding could have reacted by the time the core had melted. Some recent analyses made with more sophisticated meltdown models indicate that this extent of metal-water reaction could be less. Melting of the cladding will start 50 to 100 sec after the large double-ended pipe break in the primary coolant system if there is no action of the emergency core-cooling system.¹ Extensive core melting will occur within 10 to 60 min after the pipe break, and the debris will fall into the bottom of the pressure vessel. In another 20 to 60 min, this debris will probably melt through the pressure vessel and fall into the containment vessel, where additional metal-water reaction could take place. During this meltdown process, steam explosions could possibly occur that could result in damage to the containment vessel. Steam explosions are very complex, and more work is necessary before they are well understood. However, it appears that the contribution of the metal-water reaction to the destructive nature of these explosions is negligible.

To get a better understanding of the metal-water reaction during the meltdown process, experiments are needed to understand the fuel rod melting and collapse process, the modes of the core redistribution, failure of the core support plate and pressure vessel, etc.¹ Extensive experimentation would be required for this, and the potential benefits should be evaluated before undertaking such a program.

4.6 Hydrogen-Air Reaction in Loss-of-Coolant Accidents

It is possible for hydrogen to be produced in a loss-of-coolant accident from the metal-water reaction and from the radiolysis of the

water used in the emergency core-cooling systems. It is assumed for safety analyses for the power reactors that this hydrogen will burn as it leaves the primary cooling system or that it is always below its flammable limit. Thorough evaluation of the hydrogen-air reaction was not considered as a part of this report, but it was reviewed sufficiently to identify some of the problems associated with this reaction. There is a question about the possibility of hydrogen produced by the metal-water reaction in the lower part of the core being absorbed by the hot cladding in the upper part of the core. Some data³³ indicate that although zirconium can absorb hydrogen at higher temperatures, higher pressures are required for this to take place. Also the presence of water vapor in the gas or oxygen in zirconium will reduce this absorption greatly.

The flammability and detonation limits and the spontaneous ignition temperatures used in most safety analyses are those reported by Shapiro and Moffette.⁷⁴ Effects of the vessel size and of diluents such as steam and nitrogen on these limits are not clearly understood. It appears that increasing the vessel size will lower the spontaneous ignition temperatures, but adding diluents such as nitrogen and steam will increase them.

Pocketing of hydrogen within the containment vessel is of concern. At present, the reactor manufacturers do not assume that it will pocket, but it apparently did in the EBR-II transfer air lock.⁴³ This results in the question of the possible pocketing of the hydrogen by the buoyant forces due to the difference of the molecular weights of hydrogen and air and thermal effects versus the mixing of hydrogen and air by diffusion and forced and natural convection.

In general the reactor manufacturers argue strongly against filling the containment vessels with nitrogen, because this would make access to the containment vessel more difficult and expensive. Further they feel that the more difficult and expensive access would result in a less-safe overall situation.

5. RECOMMENDATIONS

As shown in the conclusions much is known about the rate and the extent of the metal-water reaction in reactor accident situations, but there are still some unknowns that warrant investigation. The more important of these items are listed below in a suggested order of priority.

1. In an experiment simulating the loss-of-coolant accident conditions,⁴² it was found that a fuel pin could fragment even without any melting. This makes the criterion of negligible metal-water reaction as a result of emergency core cooling difficult to interpret quantitatively. This fragmentation appears to be due to the metal-water reaction of the cladding during the experiment,⁴³ although it is recognized that the temperature-time history of the fuel pin and the oxidation of the cladding are not independent of each other. More work is needed to resolve this situation.

2. The possible pocketing of hydrogen in containment vessels should be investigated further, since it apparently did occur in the EBR-II transfer air lock. This should include the buoyancy effects, such as those due to the difference of the molecular weight of hydrogen and air and the temperature difference of hydrogen and air, and also mixing effects, such as those of diffusion and forced and natural convection.

3. The entire question of the hydrogen-air reaction needs further investigation. Because of time limitations, the literature was not searched thoroughly regarding this problem; however, a number of uncertainties were revealed. These include the effect of the vessel size and diluents, such as nitrogen and steam, on the flammability limits, the detonation limits, and the spontaneous ignition temperatures. Also the subject of detonations in large containment vessels should be investigated thoroughly if it is determined that detonations in these large vessels could occur.

4. More work is necessary to determine the effects of nuclear excursions resulting in fission energy inputs to the fuel such that the peak fuel enthalpy is greater than 280 cal/g UO_2 . The metal-water

reaction is only one of the subjects for study, and probably a minor one. Pin fragmentation, the conversion of fission energy into mechanical energy, and the dissipation of the mechanical energy in the reactor system should be studied, and these studies may lead to heat transfer and hydraulic studies that could be influenced by the reactor period and the temperature, pressure, and flow rate of the water surrounding the fuel pin.

5. Although the metal-water reaction appears to contribute little to steam explosions, it is suggested here that more work be directed to the subject of steam explosions. This appears to be a fairly complex subject area involving the fragmentation of the molten material and methods of energy transfer from the molten material to the water.

6. The possible absorption of hydrogen by zirconium at high temperatures (above 1000°C) should be investigated further. There is some evidence³³ that this does not happen unless the pressures in the reactor are higher than those predicted to be in the reactor for a loss-of-coolant accident situation. Also the presence of water in the gas or oxygen in the metal tends to inhibit this absorption.

7. A small-scale effort should continue on the meltdown behavior of the reactor core, including the effects of the metal-water reaction to determine whether there is a feasible alternate method for protecting against a loss-of-coolant accident. It should be remembered that this is a very complex subject, and the potential benefits should be weighed against the extent of the experiments.

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APPENDICES

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Appendix A

REVIEW COMMITTEES

ORNL Review Committee

T. E. Cole
M. J. Kelly
R. E. Meyer
R. C. Olson
G. M. Watson

AEC Review Committee

H. L. Hamester, RDT
A. B. Holt, DRL

External Review Committee

L. Baker, Jr., Argonne National Laboratory
D. L. Morrison, Battelle Memorial Institute
J. M. Waage, Phillips Petroleum Company

Appendix B

COMPANIES AND INSTALLATIONS VISITED REGARDING
INFORMATION FOR THIS REPORT

<u>Company or Installation</u>	<u>Individuals Contacted</u>	<u>Dates of Visit</u>
AEC, Germantown, Maryland	H. L. Hamester R. J. Impara S. J. Lanes T. G. Schlieter	9-21-66
Combustion Engineering, Inc., Windsor, Connecticut	V. C. Hall J. R. Parrette W. K. Wilhelm L. M. Johnson F. Bevilacqua J. M. West R. L. Hoover P. C. Zmola J. R. Dietrich A. Nelson	9-22-66 9-23-66
General Electric Company (meeting at ORNL)	R. McWhorter J. Smith	9-29-66
Argonne National Laboratory, Argonne, Illinois	L. Baker, Jr. J. C. Hesson R. C. Liimatainen R. E. Wilson	11-8-66 11-9-66
Battelle Memorial Institute, Columbus, Ohio	D. L. Morrison J. M. Genco	11-10-66
Westinghouse Electric Corp., Pittsburgh, Pennsylvania	R. A. Dean J. D. McAdoo R. A. Wiesmann T. Paxton	11-15-66 11-16-66
Babcock & Wilcox Company, Lynchburg, Virginia	J. H. Taylor H. Flora C. E. Parks	11-21-66
Phillips Petroleum Company, Idaho Falls, Idaho	J. M. Waage S. E. Jensen C. S. Miller R. P. Rose J. E. Grund W. Little W. H. Burgus C. Gilmore F. Bradburn P. Six D. Monnie C. Cooper	12-12-66 12-13-66 12-14-66

<u>Company or Installation</u>	<u>Individuals Contacted</u>	<u>Dates of Visit</u>
General Electric Company, San Jose, California	A. P. Bray	12-15-66
	P. W. Ianni	12-16-66
	L. F. Epstein	
	W. A. Sutherland	
	J. Hench	
	M. Siegler	
	F. J. Moody	
General Electric Company, Cincinnati, Ohio	E. Wood	
	J. F. White	12-20-66
Westinghouse Electric Corp., Pittsburgh, Pennsylvania	R. A. Dean	12-21-66
Argonne National Laboratory, Argonne, Illinois	R. O. Ivins	9-27-67
	R. E. Wilson	
General Electric Company, San Jose, California	A. P. Bray	9-28-67
	P. W. Ianni	9-29-67
	D. J. Liffengren	
	L. F. Epstein	
	W. L. Stiede	
Westinghouse Electric Corp., Pittsburgh, Pennsylvania	R. A. Dean	11-16-67
	C. J. Kubit	11-17-67
	D. Paddleford	
	T. Paxton	
	J. S. Moore	
	J. Dorycott	
	J. D. McAdoo	
	R. Salvatori	