

High temperature chemistry for the analyses of accidents in nuclear reactors

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Abstract - This paper describes some of the demands which the analysis and prediction of the consequences of faults and accidents in nuclear reactor systems makes on our knowledge and understanding of the high temperature chemistry of the fuel and other materials. We illustrate these demands by describing, for a Pressurized Water Reactor, the chemistry of the fuel clad gap, of the evolution of degradation of the core, and of the reaction between the material of the degraded core and concrete. For a liquid metal cooled fast breeder nuclear reactor, we take examples from the chemistry of the reactions between liquid sodium and fuel, and aspects of the determination of the equation of state of the oxide fuel for temperatures up to ca. 5000K.

INTRODUCTION

In this paper we shall consider some of the demands which the analysis and prediction of the consequences of faults and accidents in nuclear reactor systems makes on our knowledge and understanding of the high temperature chemistry of some of the relevant materials.

We shall discuss some chemical aspects of the analysis and consequences of (1) faults in which the engineered design features can be relied upon to ensure that the system can continue in operation or be readily shut down and of (2) accidents in which the ability to transfer heat from the nuclear core of the reactor to the coolant is lost.

The types of reactor with which we shall be concerned are the pressurised water reactor (PWR) and the liquid sodium cooled fast breeder reactor (FBR). For a typical PWR with an electrical output of 823 MW(E), the amount of fuel - enriched uranium dioxide - will be ca. 80 tonnes, of Zircaloy cladding 16.5 tonnes, and of other materials such as stainless steel 6.5 tonnes. The average burn-up of the actinide elements will be between 2 and 3%. The coolant is water at 557-559K and at a pressure of ca. 15.8 MPa. We shall essentially be concerned with the chemistry of the PWR fuel - the 'so-called' rods of uranium dioxide clad in Zircaloy (zirconium with ca. 1.5 wt.% tin). We shall consider the evolution of the chemical constitution of the fuel under irradiation together with some effects of the radiation on the chemical speciation within the fuel clad gap and the implications regarding the compatibility between fuel and cladding material. The distribution of fission product elements obtained from the thermal fission of ²³⁵-uranium and ²³⁹-plutonium together with that for fast fission of ²³⁹-plutonium is shown in fig. 1. The consequences of the failure of the cladding would result in the presence of some of the fission product elements and fuel in the water of the primary circuit. We need to consider such behaviour in the analysis of the consequences of design basis faults.

In PWRs, there are safety provisions which would ensure that the core of the reactor is adequately cooled. The possibility that these provisions should fail to cool the core is very remote, but in such an event the core would heat up, the geometry of the core would be lost, and it might melt. Such a consequence has been defined as a 'degraded core accident' and the consequences of such an accident can be very damaging. Much of the information that we shall discuss has been obtained following the accident in the United States of America to the PWR (Babcock and Wilcox) - Three Mile Island, Unit 2 in March 1979; much effort has been given to the prediction of the possible releases of radioactivity in such accidents. It should be

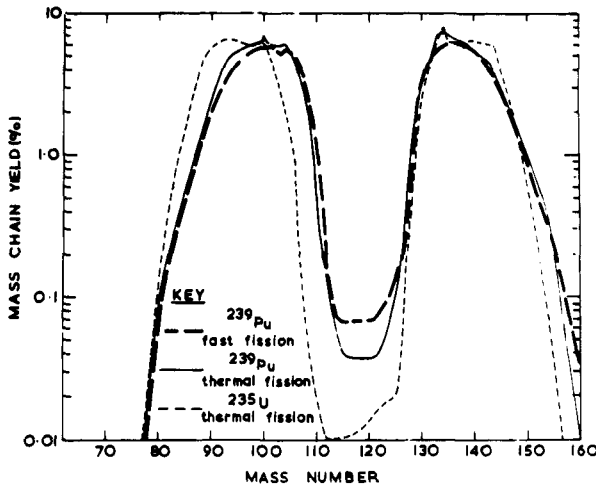


Fig. 1 The fission yields for ^{235}U and ^{239}Pu

remembered that the consequences of the accident at Three Mile Island were essentially limited to severe damage to the plant. In the United Kingdom, the releases or source terms of radionuclides for various sequences of severe accidents of low probabilities for the proposed PWR (Westinghouse) at Sizewell have been estimated. It is beyond the scope of this paper to discuss aspects of Probabilistic Safety Assessment (PSA); the methodology for the estimation of the probabilities of such events. An excellent description of this methodology has been given for the U.K. Sizewell PWR by Gittus (ref. 1). The probability that the core of a modern PWR would melt and the reactor containment would fail is very low: 7×10^{-8} per year.

The accident in the Soviet Union in April, 1986 at Chernobyl was a degraded core accident in a boiling water, graphite moderated, pressure tube reactor (Unit 4). The details of this accident and some preliminary analyses have been described in a recent publication of the International Atomic Energy Agency (ref. 2). Some of the radionuclides which were considered in Nuclear Regulatory Commission's Reactor Safety Study - consequence analysis for Light Water Reactors are given in Table 1 (ref. 3) and provide the basis for detailed analysis of their species and fate.

For the liquid sodium cooled fast reactor (FBR) there are two basic designs. The liquid sodium coolant operates over a range of temperatures from $350^\circ - 600^\circ\text{C}$. In the French, British and Soviet designs the pumps for the sodium in the primary circuits and the heat exchangers for the primary and secondary sodium circuits are located in one pool, whereas in the German design for SNR-300, there are three parallel heat transfer loop systems.

TABLE 1. Radionuclides which have been considered in consequence analysis for degraded core accidents in light water reactors (ref. 3)

Element	Radionuclide	Element	Radionuclide
Cobalt	^{58}Co , ^{60}Co	Iodine	^{131}I , ^{132}I , ^{133}I , ^{134}I , ^{135}I
Krypton	^{85}Kr , $^{85\text{m}}\text{Kr}$, ^{87}Kr , ^{88}Kr	Xenon	^{133}Xe , ^{135}Xe
Rubidium	^{86}Rb	Caesium	^{134}Cs , ^{136}Cs , ^{137}Cs
Strontium	^{89}Sr , ^{90}Sr , ^{91}Sr	Barium	^{140}Ba
Yttrium	$^{90\text{Y}}$, $^{91\text{Y}}$	Lanthanum	^{140}La
Zirconium	^{95}Zr , ^{97}Zr	Cerium	^{141}Ce , ^{143}Ce , ^{144}Ce
Niobium	^{95}Nb	Praseodymium	^{143}Pr
Molybdenum	^{99}Mo	Neodymium	^{147}Nd
Technetium	$^{99\text{m}}\text{Tc}$	Neptunium	^{239}Np
Ruthenium	^{103}Ru , ^{105}Ru , ^{106}Ru	Plutonium	^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu
Rhodium	^{105}Rh	Americium	^{241}Am
Tellurium	^{127}Te , $^{127\text{m}}\text{Te}$, ^{129}Te , $^{131\text{m}}\text{Te}$, ^{132}Te	Curium	^{242}Cm , ^{244}Cm
Antimony	^{127}Sb , ^{129}Sb		

The fuel in the core of a fast reactor is essentially a solid solution of uranium dioxide and plutonium dioxide. The fuel is in the form of pellets clad in stainless steel. The breeder elements consist of pellets of uranium dioxide clad in stainless steel. For the planned UK Commercial Demonstration Fast Breeder Reactor (CDFR); the electrical output will be ca. 1250 MW(E) and the total plutonium inventory will be ca. 3 tonnes and that of uranium will be ca. 24 tonnes. For this system much consideration has been given to the consequences of failure of the fuel cladding and to the consequences of a significant loss of the capability to remove heat. Here, we shall consider some aspects of the failure of the fuel cladding and loss of coolant which could lead to severe overheating of a core.

We have also carried out analyses of the source term in the primary containment of CDFR for hypothetical core descriptive accidents (HCDA) (Holloway et al (ref. 4)). In accidents involving loss of coolant flow and with no trip of the reactor, boiling of the sodium would occur within ca. 20 seconds of initiation and would be followed by voiding of the central core. This loss of the liquid phase or voiding would cause an increase in reactivity which would be followed by disruption of the core within ca. 25 secs. The temperatures in the core can reach ca. 5000K, and for this reason there has been very much interest in the formulation of equations of state for the materials of the reactor core up to very high temperatures. The materials which have been considered are the fuel, the coolant and stainless steel. Indeed, the extensive studies on the determination of the vapour pressures of uranium and uranium-plutonium solutions up to temperatures above 5000K will be described by Ohse (ref. 5) in another plenary lecture to this conference. The ingress of energy under some accident conditions can be very rapid and then thermal equilibrium in the system would not be attained. There is considerable interest in the role of the volatile fission product elements, the noble gases and caesium in the description of fuel and core in accident conditions.

We shall now discuss some specific aspects of the behaviour of fuel and fission product elements in both types of reactor system during fault and accident conditions.

PRESSURISED WATER REACTOR (PWR)

Chemistry of the PWR core

The chemical constitution in the fuel clad gap and the influence of radiation on the chemical state of the fission products may be of significance in understanding the mechanism of failure of the Zircaloy clad by stress-corrosion cracking.

Where the cooling of the fuel rods in the core is lost the Zircaloy will react with steam to produce hydrogen, further heating would result in the reaction between fuel and Zircaloy with the corresponding loss of the integrity of the cladding and loss of the more volatile species of the fission product elements into an atmosphere containing steam and hydrogen. The surface area of the pipework of the primary circuit is large and many of the released fission product species could react or deposit on the surfaces of the primary circuit and others could form aerosol material. Much attention has been given to the behaviour of the volatile fission product elements, caesium, iodine and tellurium (refs. 6-9).

The result of the loss of coolant could finally lead to the melting of the core including the structural members of stainless steel and Inconel. Such a mixture would be a source of volatile material which could condense to form aerosol particulate material. The material of the molten core could melt through the stainless steel pressure vessel and react with the concrete of the containment vault. In addition to the fuel there are control rods - an alloy of silver, cadmium and indium clad in stainless steel and burnable poisons - borosilicate glass clad in stainless steel.

The analysis of degraded core accidents requires a detailed assessment of the likely chemical constitution of the materials of the core, particularly the irradiated fuel, in the conditions of the fault or accident and an analysis of the fate of the vapour species many of which will condense and react with surfaces or form aerosol particulate material. Some of the important chemical reactions and the temperature at which they occur are shown in Table 2.

TABLE 2. Melting sequence and pattern of the degradation of a PWR core

Temperature of cladding surface (°C)	Phenomenon
700-750	Borosilicate starts to soften. Incipient melting of Ag-Cd-In alloy inside control rods.
800	Fuel rods start to swell and burst and release some fission product species and fuel to the primary circuit.
900	Reaction between Zr and steam starts. Temperatures of fuel rods rise more rapidly.
1300-1500	First visible liquid formation due to (1) Inconel grid-Zircaloy eutectic reaction, and (2) UO ₂ -Zircaloy reaction or exposed internal clad surfaces. Reaction 2 can result in vaporisation of fission product species.
Above 1500	Further heating of exposed fuel results in the loss due to vaporisation of the volatile fission product species.
1850-1950	Zircaloy starts to melt; subsequent behaviour is governed by thickness of ZrO ₂ layer. Thin oxide layer - Zr melting and Zr + UO ₂ reaction. Thick oxide layer - internal Zr surface may be protective and melting delayed.
2400-2650*	ZrO ₂ and UO ₂ -ZrO ₂ mixtures melt.

*At the highest temperatures vaporisation of the less volatile fission product species has to be considered.

Chemical constitution of irradiated PWR fuel

The fuel for a PWR is essentially stoichiometric uranium dioxide. The conditions under which the fuel operates result in fuel centre temperatures of ca. 1200°C. At these temperatures, the irradiated fuel will be essentially a solid solution of the fission product elements in the fluorite structured lattice of the oxide. The average valency of the fission product elements and cations will be less than four and some oxidation of the U⁴⁺ ions to U⁵⁺ ions will occur resulting in an increase in the thermodynamic oxygen potential of the fuel matrix with increasing burn-up of the actinide atoms. Such an increase in oxygen potential would only occur providing that there be no transfer of oxygen from the fuel matrix to the Zircaloy cladding (ref. 10). During the conditions of normal operation, there will be a small amount of fission product elements in the fuel-cladding gap which will originate from athermal processes such as fission spikes and recoil and it will be due to power transients that there would be an enhancement of the amount of fission product species within the gap. The most volatile fission product elements are the noble gases, krypton and xenon which, like the added helium gas, probably remain chemically inert. Helium is added to improve the thermal conductivity within the gap. The other volatile fission product elements are caesium, rubidium, iodine, bromine, selenium and tellurium. We shall see that the presence of helium can play a significant role in the behaviour of iodine in a radiation field. We have calculated the variation with oxygen potential of the chemical constitution of the fuel-cladding gap (ref. 11), using the computer program SOLGASMIX (ref. 12) which calculates the phase assemblage of the system with the minimum value of the total Gibbs energy. For the assessment of the chemical constitution of Cs, I and Te (Rb, Br and Se have not been considered separately because their yields are low) in the presence of uranium dioxide (UO_{2+x}), the quantity of fission product elements taken is 1 percent of their total inventory at a temperature of 650°K. For this assessment of the chemical constitution of Cs, I and Te with UO₂, we need information about the thermodynamic quantities of the condensed and gaseous species phases which could be present. The compounds and gaseous species which have been considered are CsI(c) CsI(g), Cs₂I₂(g), Cs(c), Cs(g), Cs₂(g), Cs₂Te(c) and Cs₂Te(g). The ternary condensed phases considered were Cs₂UO₄, Cs₂U₄O₁₂ and Cs₂U₄O₇. The data for these were mainly taken from a current assessment (refs. 13, 14). The model used for the UO_{2+x} phase was that developed by Lindemer and Besmann (ref. 15). In Fig. 2 we give the pressures in the gap

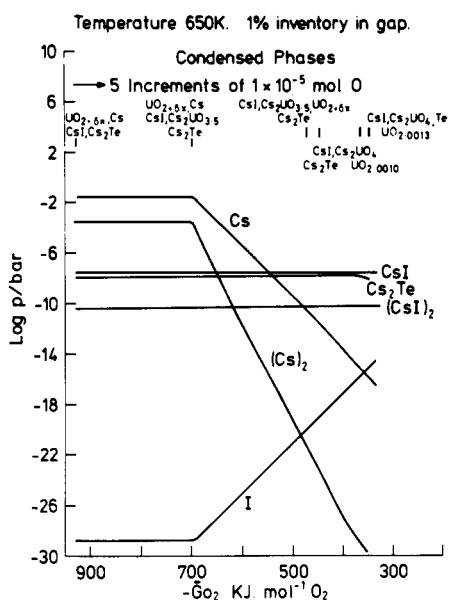


Fig. 2. The chemical constitution of the fuel-clad gap of a PWR rod at 650K.

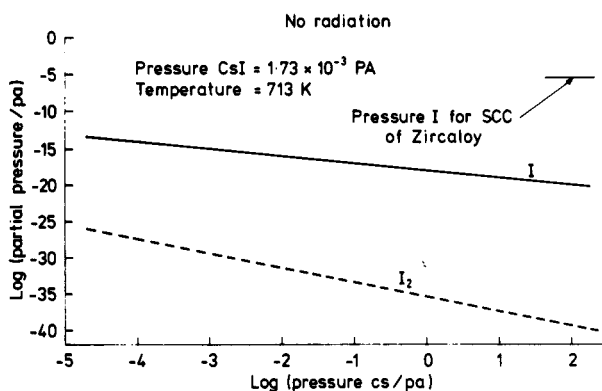
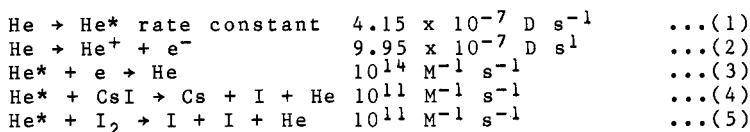


Fig. 3. The thermal equilibrium for the decomposition of CsI gas at 713K.

and the plenum of the fuel rod for the major species, and also the condensed phases at increasing amounts of oxygen. The major point to note is that the potential of iodine increases with increasing oxygen potential (-700 kJ.mol⁻¹) but the pressure is considerably lower than that of CsI. The pressures of iodine are below those which would cause stress corrosion cracking of the Zircaloy cladding by these thermal reactions.

Under reactor operating conditions, we can expect gas concentrations to be greatly changed from those at thermal equilibrium because the large continuous input of radiation energy, largely in the form of fission fragment radiation tend to dissociate molecules into neutral atoms or ions. This has been recognised by Konashi et al (refs. 16,17) and some expected features of the processes, such as the dependence of the presence of iodine atoms on the square root of the dose-rate in a mechanism containing recombination as the ultimate fate of transient species has been suggested by Kanno et al (ref. 18).

An important aspect of the behaviour not hitherto discussed is that we are dealing with a dilute mixture of other gases in helium. Helium is well known for greatly sensitising the radiolytic decomposition of minor components of its mixtures (ref. 11). This occurs by way of charge and energy transfer from its highly energetic ion He⁺ and metastable atomic states 2³S and 2¹S. All of these species will take part in inelastic collisions with gas phase molecules, including CsI and I₂, easily dissociating them. The kinetic simulation of the chemistry was simplified by assuming that all He⁺ ions recombine with electrons efficiently to form excited metastable atoms. The reactions may be represented as follows where D is the dose rate in w.g⁻¹.

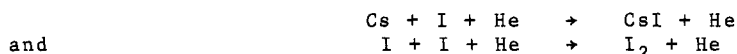


The rate constants of reactions 1 and 2 (k₁ and k₂) were obtained from the G values (species per 100 eV) for He⁺ and He* which are 2.4 and 1.0 respectively (ref. 19) and we assume that the effect of radiation type (ref. 20) can be neglected. The rate constant k₁ is thus

$$k_1 = 4DG(\text{He}^*) \times 6.242 \times 10^8 / 6.022 \times 10^{25}$$

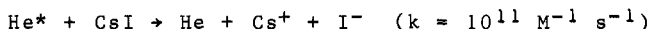
*4 is the atomic weight of helium, 6.242×10^{18} is the number of eV per J, 6.022×10^{25} is Avogadro's number × 100.

with $G(\text{H}^+)$ replacing $G(\text{He}^*)$ for k_2 . The total dose rate was 21.6 wg^{-1} [1.6 wg^{-1} from neutron and gamma radiation and 20 wg^{-1} as an estimate for fission fragments]. The ionic recombination rate constant for reaction (3) is typical for its class (ref. 22) and taken to be temperature insensitive, as are the simple bimolecular rate constants for reactions (4) and (5). These reactions will modify the effect of the existing thermal equilibria; examples of the thermal reactions are



The combined effect of all the reactions will cause a new dynamic equilibrium to be established quickly where we expect the steady state concentrations of atoms to be greater than in the absence of radiation.

Burns et al (ref. 11) computed the influence of radiation on the equilibria in the gap using the FACSIMILE program (ref. 23) which formulates and solves numerically the necessary differential equations in species concentrations with respect to time when the reactions, rate constants, and starting concentrations are provided. For the example given, the mean gap temperature was 713 K and assumed the partial pressure of CsI vapour to be that in equilibrium with the solid at 650 K, the assumed cladding surface temperature, and we have made variations in the partial pressure of Cs. Fig. 3, shows the variation of I and I_2 pressures with partial pressure of Cs in the absence of radiation. Fig. 4, shows how the computed partial pressures for reactants, except those of He and CsI which remain virtually constant vary with the Cs pressure in the radiation field. These calculated pressures of iodine are considerably greater than those quoted by Konashi et al (ref. 17) as the threshold for iodine to cause stress corrosion cracking of the Zircaloy clad. The effect of ionic reactions was also considered, for example, reactions such as



The rate constants were estimated as typical of their types, which are charge transfer, dissociative positive ion - molecule reactions, dissociative and non-dissociative electron capture, and recombination with electrons or with negative ions.

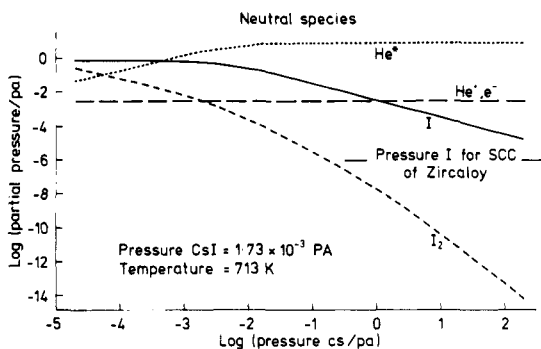


Fig. 4. The neutral gaseous species from the decomposition of CsI in the radiation field of the fuel-clad gap at 713K.

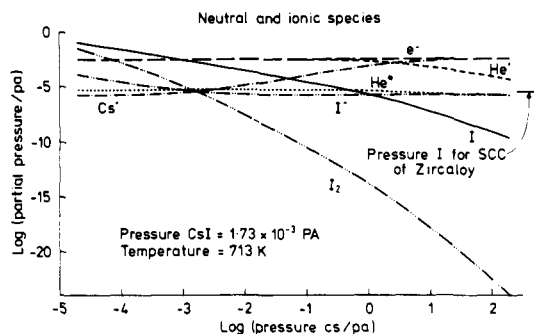


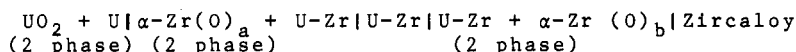
Fig. 5. The neutral and ionic species from the decomposition of CsI in the radiation field of the fuel-clad gap at 713K.

The final effect of all these reactions is shown in Fig. 5 in which it is seen that the stronger tendency towards recombination in the condition where ionic dissociation is considered causes lower calculated concentrations of I, however the concentrations of I will again be greater than without the radiation field. In this work, wall effects and the participation of a number of other potential species and reactions are neglected. Species include Cs_2 and Cs_2I_2 and reactions include those with Xe. As well as displacing the thermodynamic equilibria of the gas phase, it must be also conceded that the effect of such high radiation dose rates may also disturb condensed phase equilibria.

Evolution of the degradation of the core

The fuel matrix and the cladding are barriers to the release of fission product elements to both the gap and the coolant. If the fuel were to heat up due to loss of cooling then both fission product elements would diffuse from the fuel matrix onto the grain boundaries where they would form bubbles. Interlinking of the bubbles would result in loss of the fission product elements from the fuel. A considerable amount of work has been carried out on understanding the behaviour of the noble gases; such studies have been reviewed by Matzke (ref. 24); some of the volatile elements caesium, iodine and tellurium which may not dissolve readily in the lattice of the fuel may be found in the bubbles and would be released when there are paths for release and the temperatures are sufficiently high. There have been many studies of the release of Cs, I and Te from irradiated fuel and simulated irradiated fuel up to temperatures above 2000°C. Olander (ref. 25) has discussed the diffusion of the fission product elements in the UO_2 lattice in a controlled atmosphere between 1000 and 2000°C. Experiments have been carried out on irradiated fuel and measurements have been made of the variation of extent of release of fission products with temperature and time into hydrogen-steam atmospheres (ref. 7). Such data are required to predict the consequences of the loss of coolant and integrity of the cladding. There has been much discussion of the chemical form in which the fission products are released into the hydrogen-steam atmospheres.

Some of the chemical changes which occur during degradation of the core have already been listed in Table 2. We note that the reaction which can result in the loss of integrity of the cladding starts at 900°C, that between Zircaloy and steam and that between unoxidised Zircaloy and UO_2 fuel starts at 1300-1500°C. In the absence of direct contact between UO_2 and Zircaloy, oxygen can only be transported from the fuel to the cladding through the gas phase. Without externally applied pressure, no reaction has been observed between UO_2 and Zircaloy at temperatures up to 1500°C since there was no physical contact between pellets and zircaloy cladding of fuel rods; the minimum solidus temperatures in the U-Zr-O ternary phase diagram are at ca. 1300°C (ref. 26). A detailed study of the reactions between UO_2 and Zircaloy has been reported by Hofmann and Kerwin-Peck (ref. 27). The sequence of reactor layers at the interface between the reactants which is observed at room temperature is



$\alpha-Zr(O)_a$ and $\alpha-Zr(O)_b$ are $\alpha-Zr$ with dissolved oxygen in two different 2-phase regions separated by a U-Zr alloy single phase region.

In general the number of reaction layers and their sequence is the same for all temperatures and reaction times. A very elegant analysis of the UO_2 -Zr couple in terms of the U-Zr-O phase diagram and the transport properties of the system has been given by Olander (ref. 28). The analysis was carried out for 1500°C and accounted for the uranium rich alloy sandwiched between the two $\alpha-Zr(O)$ layers, the sequence of phases and the kinetics of layer growth. The diffusion path is shown in Fig. 6.

Some further work is required on the UO_2 -ZrO₂ section of the phase diagram. Some preliminary attempts have been made to model these phase relationships by Imoto (ref. 29) together with some further experimental studies of the phase diagram by Yamanaka et al (ref. 30). A significant feature of these reactions is that an appreciable amount of UO_2 up to 9 vol.% (Hofmann and Kerwin-Peck (ref. 28)) can be dissolved by Zircaloy-4. In a fuel rod complete release of the volatile fission product from the molten fuel region can be expected. The presence of simulated fission product elements Cs, I and Te did not significantly influence the reaction of UO_2 and Zircaloy although Te had reacted with the Sn of the Zircaloy (ref. 27).

As the core of the reactor heats up and the integrity of the cladding is lost the volatile fission products will be lost from the fuel at a quite early stage of the degradation. The volatile fission products have been given earlier as Cs, Rb, I, Br, Te and Se. Most of the fission product elements will remain with the core debris; as the fuel heats up phases of the fission product elements will nucleate. The core debris will ultimately consist of two immiscible liquid phases; one an oxide and the other a metallic phase. A detailed knowledge of the speciation of the volatile fission products in mixtures of steam and hydrogen for the various

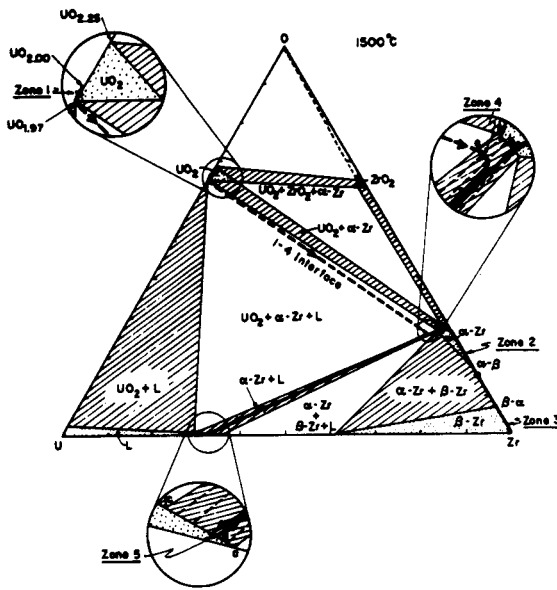


Fig. 6. The diffusion path for the Zr- UO_2 reaction on a section of the U-Zr-O phase diagram at 1500°C (ref. 28).

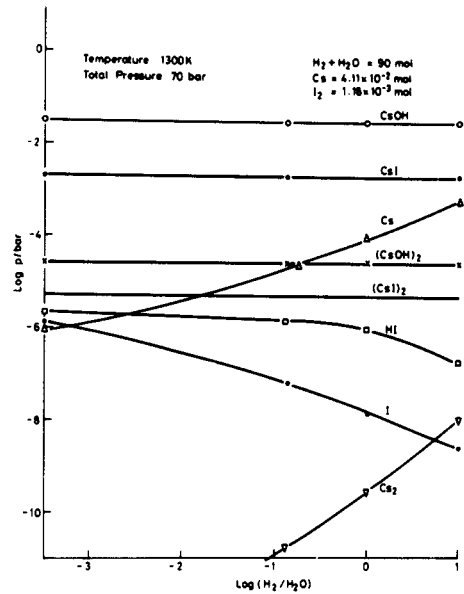


Fig. 7. The gaseous species of Cs and I in the hydrogen-steam mixtures at 1300K .

conditions of temperature, total pressure, and relative amounts of steam and hydrogen. The speciation of caesium and iodine in various mixtures of steam and hydrogen has been calculated and the variation of the partial pressure of the various species with the composition of the steam-hydrogen mixtures is shown in Fig. 7 for a temperature of 1300K and a total pressure of 70 bars (Potter et al (ref. 32)). The predominant Cs containing gaseous phases are CsOH , CsI and Cs ; Cs_2Te was not included in these calculations. The quantities of elemental I gas and HI gas under these conditions are very small. The Cs containing species will react or condense on surfaces and also form considerable quantities of material in the form of aerosol particles. The behaviour of caesium containing species with surfaces and in aerosol form has been a significant feature of many studies (refs. 6,8). The small quantities of gaseous I and HI would interact with structural materials. The quantification of the removal processes with these fission products is an important part of the research programme on severe accident analysis. A possible source of volatile iodine is the formation of gaseous HI by the reaction of CsI with boric acid (ref. 31), the boric acid is present in the primary coolant.

The behaviour of tellurium is complex and there are several aspects which need detailed examination. Previous assessments (ref. 32) have indicated that whilst tellurium would be present as Cs_2Te in the condensed phase, it would decompose into the elemental components when vaporization occurred; however, recent determinations of the vapour pressure up to 1000K (ref. 33) suggest that Cs_2Te vaporises congruently and that $\text{Cs}_2\text{Te}(\text{gas})$ is the predominant species. Observations suggest that at higher temperatures some CsTe is found (refs. 34,35) and Cs is the predominant gas phase species (ref. 35). The speciation in the gas phase of elemental tellurium in mixtures of hydrogen and steam has been described (refs. 32,35) and the major species are Te_2 , Te , H_2Te , and TeOH ; TeOH is only significant at high oxygen potentials.

There have been studies of the reactions between tellurium and stainless steel in order to quantify the deposition processes which could occur within the primary circuit of the reactor. Oxidation of Zircaloy prevents the reaction of gaseous elemental tellurium species to form Zr tellurides. The thermodynamic tellurium potential for the formation of ZrTe_2 (ref. 36) is higher than that for the formation of Cs_2Te (ref. 14). If reaction of elemental tellurium or of $\text{H}_2\text{Te}(\text{gas})$ did form Zr tellurides, then subsequent oxidation would result in the Te becoming associated with the tin of the Zircaloy. Tin will not oxidise in the conditions which prevail during the degradation of the core; the reaction product SnTe vaporises congruently and it is suggested that this compound is the major Te gaseous species under some conditions.

There are data available on the phase relationships of the systems Cs-Te (refs. 37,38), Zr-Te (ref. 39), Sn-Te (ref. 40) as well as for the systems Cr, Ni and Fe with Te (refs. 41-45). A detailed assessment of the thermodynamic data and phase equilibria of these systems is, at present, being carried out by the author.

In addition to the fission product elements, cadmium from the control rods will volatilize and form aerosol material and provide an additional large amount of surface on which material volatilized at a slightly later time could condense.

Vaporization of the fission product species, such as those of the actinides, lanthanides, Ba, Sr and Ru, will occur from mixtures of molten fuel, Zircaloy and structural components - the core debris. The most volatile species of these elements would be the hydroxides. Further experimental studies on the gaseous hydroxide species to support the assessments of their thermodynamic properties (refs. 46,47) are required.

There are a number of gaseous molecules such as Cs_2MoO_4 (ref. 48), Cs_2CrO_4 (refs. 49,50) which could contribute to the releases of Cs and Mo; evidence has also been presented for the existence of the gaseous molecule Cs_2TeO_3 (ref. 51). It is important to ensure that all major species which could contribute to the loss of fission product elements from the core debris are characterized and their thermodynamic properties measured.

Interactions of core debris and concrete

If the debris formed from the core materials were to melt through the reactor pressure vessel, reactions of this debris with the concrete of the containment would occur (ref. 52). The chemical changes which occur during such reactions are the decomposition of the concrete giving both water vapour and carbon dioxide (ref. 53). The sparging or streaming of these gases through the molten material can result in the formation of aerosols from the debris. These reactions could be an important source of radionuclides to the cavity and containment atmospheres during a severe accident in a light water reactor (refs. 54-56). As the bubbles rise through the molten debris, the gas within them will undergo a change in composition due to reduction of CO_2 (gas) and H_2O (gas) by some of the metals (especially any unoxidised Zr) and some gaseous species which evaporate from the surface of the bubbles will also be found within these bubbles. These latter species could be the main source for the formation of aerosol material; when the bubbles break through the surface of the pool many of the gaseous species will condense to form aerosol particles. We are endeavouring to estimate the amount of aerosol material which could be formed and its chemical constitution. The molten debris, like that which would be present before any melting through the stainless steel reactor pressure vessel, would consist of an oxide phase and a metal phase. The configuration of the melt can influence the composition of the vapour within the bubbles.

We have considered different configurations of the debris; these are two immiscible liquids (1), (simultaneously in equilibrium with the gas phase, (2) with a metal layer above an oxide layer, and (3) with an oxide layer above a metal layer.

The oxide phase contains the fuel uranium with the other actinide oxides and the oxides of the fission product elements, these are SrO, BaO, and the lanthanide oxides together with zirconium oxide which is formed mainly from the oxidation of the Zircaloy cladding.

The metallic phase contains the stainless steel, the components of the control rods (Ag, Cd and In), and the metallic and metalloid fission product elements - Mo, Tc, Ru, Rh, Pd and some Te together with unoxidised cladding.

Additionally some dissolution of the oxide components of the concrete into the oxide of the debris would occur.

There may be times during this interaction when the sparging gas bubbles keep the two phases well mixed, resulting in globules of one phase suspended in the other. This leads to the configuration (1) above, where the bubbles may be simultaneously in contact with both the metal and the oxide phases. At other times the two phases will separate to form stable layers. The orientation of the layers oxide above metal or metal above oxide would

depend upon their relative densities. If the melt stratifies at sufficiently early times, the density of the oxide layer will be dominated by urania which will be denser than the metallic layer - the oxide layer will be below the metallic layer - configuration (2) during the interaction of the debris with concrete. The amount of the less volatile species which would be released is dependent on the configuration of the molten pool; in general, the trend in the magnitude of the release of the fuel and fission products from the different configurations of the melt is (1) (3) (2). The controlling factor in the vaporization process is oxygen potential.

The chemical constitution of the oxide layer would be continuously changed by the addition of the oxide components of the ablated concrete (in particular silica) resulting in an oxide layer of lower density than the metal; the configuration (3) above. The modelling of the vaporization of the species from the melt at various stages of the interaction was done with the code SOLGASMIX, and for the initial calculations, the three phases were considered as ideal solutions. Subsequently we have used the approach of Hastie and Bonnell (ref. 57) where association can be considered by introducing components which are the ternary phases formed in the solid phase, for example, BaZrO₃, and silicate phases. We have also simplified the systems by including only representative components; for example, La₂O₃ represents all the lanthanide oxides.

The oxide phases of concrete which we have included are CaO, K₂O, SiO₂ and FeO. The oxides from the decomposing concrete will be subsumed into the oxide phase of the debris. The initial inventory which we have taken is shown in Table 3. The conditions which we used in the calculations were taken from thermal hydraulic and heat transfer predictions for a particular accident sequence (ref. 58). At 2733K the estimated temperature for the first hour of the reaction, ca. 9000 kg of silica are subsumed into the oxide phase and ca. 1000 kg of H₂O and ca. 250 kg of CO₂ are released from the ablating concrete.

We have calculated the extent of vaporization for the different possible configurations of the molten phases after 1 hour at 2733K. Our calculations indicate that the extent of vaporization is the most significant in the first hour; the continuous dilution of the melt by the components of concrete and the decrease in the temperature of the melt with time are the major factors which lead to the decrease in vaporization. The results of these calculations show that, for each of the configurations, the more volatile fission product species such as those of Cs and Te would be released very rapidly.

The predominant gas phase species are shown in Table 4 for the configuration I - two immiscible liquids in equilibrium and well mixed.

Kinetic effects, including mass transport in the melt and in the bubbles have been discussed (ref. 54); and we showed that the equilibrium gas

TABLE 3. Initial composition (moles) of the debris

Oxide phase			
UO ₂	3.0 x 10 ⁵	SrO ₂	7.0 x 10 ⁴
SrO	7.0 x 10 ²	*SiO ₂	1.5 x 10 ⁵
La ₂ O ₃	1.0 x 10 ³	*K ₂ O	1.4 x 10 ⁴
PuO ₂	2.0 x 10 ³	*CaO	5.5 x 10 ⁴
Cs ₂ O	1.5 x 10 ²	*FeO	1.4 x 10 ⁴
Metallic phase			
Mo	3.3 x 10 ³	Cr	1.3 x 10 ⁵
Te	1.3 x 10 ²	Fe	7.9 x 10 ⁵
Zr	1.1 x 10 ⁵	Ag	1.7 x 10 ⁴

*Subsumed concrete in 1 hour at 2733K.

TABLE 4. Vaporization of species from molten debris at 2733K and 1 bar total pressure in 1 hour

Debris configuration: two immiscible liquids in equilibrium well mixed			
Element	Amount in vapour phase (moles)	Fraction of initial amount	Dominant gaseous species
Cs	313.7	0.98	Cs
Te	93.3	0.73	Te
Sr	217.1	0.31	Sr
La	105.5	0.05	LaO
Mo	6.01 x 10 ⁻³	1.8 x 10 ⁻⁶	Mo
U	10.7	5.4 x 10 ⁻³	PuO, PuO(OH)
Pu	134.0	4.6 x 10 ⁻⁴	UO ₂ , UO(OH)
Fe	42250.0	5.3 x 10 ⁻²	Fe
Cr	13080.0	0.10	Cr
Zr	13.8	7.7 x 10 ⁻⁵	ZrO
Ag	9024.0	0.53	Ag
Si	96950.0	0.64	SiO
K	25940.0	0.91	K, KOH

composition will be attained in the rising bubbles with the exception of the most volatile component, caesium.

The effectiveness of the concrete to contain the debris has been discussed in detail in terms of the heat transfer behaviour; however, the changes in chemical constitution which occur during the cooling of the pool may influence the characteristics of heat transfer. In order to understand such changes it is necessary to have a knowledge of the phase relationships between UO_2 and ZrO_2 with the major constituents of concrete namely CaO , MgO , SiO_2 , Al_2O_3 and Fe oxides. There are still uncertainties in the phase diagrams which make the assessments of the phase relationships of higher order systems imprecise. There are, however, observations on urania concrete reactions which can be used to give information about the phase relationships. An example of this type of information (ref. 59) has been provided in which the solubilities of both UO_2 and ZrO_2 in silicate melts were measured under oxidising conditions in the temperature range 1473-1823K. The study was aimed at assessing the potential of silicate rocks as sacrificial barrier materials. An important conclusion was that dissolved zirconia and urania will precipitate out and settle to the bottom of a silicate melt during cooling. Further assessments of the experimental observations of the reactions between simulated debris in terms of the phase relationships of the lower order systems are required. Some further experimental determinations of the phase diagrams for UO_2 and ZrO_2 with the oxides of concrete may be needed. We have already noted the importance of having sound thermodynamic data for the gaseous hydroxides.

FAST BREEDER REACTOR (FBR)

In this part of the paper we shall be concerned with two areas of research concerned with design basis faults and core disruptive accidents. The first topic is of relevance to both design basis faults and core disruptive accidents and considers the reaction of the fuel with the coolant and the second topic is concerned with thermodynamic quantities of the oxide fuel up to conditions of high temperature and pressure.

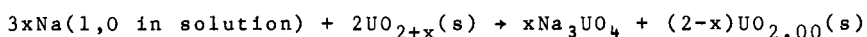
Reactions between coolant and fuel in FBR

The chemical changes which can occur on failure of the cladding of fuel pins and the consequences of such failures for the contamination of the primary circuit by fuel and fission product species have been recently reviewed (ref. 60).

In an operating fast reactor fuel pin, migration of oxygen, fuel and fission product species can occur due to the steep temperature gradients which prevail (centre temperature 2000°C , surface temperature ca. 800°C). As a result of the temperature gradients the more volatile fission product elements will be found in the colder regions of the fuel pin such as the fuel clad gap and their quantities and chemical constitution will depend on the conditions of the irradiated fuel. The possible chemical constitution of the fission product elements in fuel and breeder pins is given in Table 5. The chemical constitution of the fuel clad gap would depend on the composition of the fuel and the extent of burn-up of the heavy atoms. In addition to the compounds Cs uranoplutonates, Cs_2Te , and CsI , caesium chromates can also be formed from the cladding.

When the cladding is breached, any sodium which enters the pin could react both with the matrix of the fuel, a solid solution of urania-plutonia containing dissolved fission product cations, and with the compounds in the fuel-clad gap. Such reactions can lead to the contamination of the primary circuit. Reactions with the urania of the breeder pins have also to be considered. The reactions of liquid sodium with urania, urania-plutonia solid solutions with which we shall be concerned involve the formation of the compounds Na_3UO_4 , $\text{Na}_3\text{U}_{1-x}\text{Pu}_x\text{O}_4$; their formation could result in considerable swelling of the pellets of fuel or breeder with the further opening of the breached region of the cladding and greater exposure of the surfaces of the fuel to liquid sodium.

We shall now discuss some aspects of the reactions between liquid sodium and urania and urania-plutonia solid solutions. An isothermal section of the ternary phase diagram is shown in Fig 8, and the equilibrium phase field of major interest is that containing $\text{UO}_2(\text{s})$, $\text{Na}(\text{l}, \text{O in solution})$, and $\text{Na}_3\text{UO}_4(\text{s})^*$. The overall reaction involving hyperstoichiometric urania can be represented by



* (s) and (l) represent the solid and liquid state

TABLE 5. The chemical state of fission products in irradiated urania breeder and urania-plutonia solid solution fuel

Fission product elements	Likely chemical state
Kr, Xe	Elemental state.
Y, La-Eu and actinides	Oxides which dissolve in host matrix.
Ba, Sr	Oxides which can dissolve to a limited extent in the fuel and also form separate phases $Ba_{1-x}Sr_x[Zr_{1-w-y-z}Mo_wU_yPu_z]O_3$.
Br, I	Single phase halide solution. $Cs_{1-x}Rb_xBr_{1-y}I_y$
Rb, Cs	$Cs_{1-x}Rb_xBr_{1-y}I_y$ and compounds analogous to Cs_2UO_4 and $Cs_2UO_{3.5}$, eg $(Cs_{1-x}Rb_x)_2(U_{1-y}Pu_y)_O_4$
Se, Te	Single phase chalcogenide solution. $(Cs_{1-x}Rb_x)_2Sr_{1-y}Te_y$.
Zr, Nb	Some dissolution in host matrix, see also Ba, Sr group.
Mo, Tc, Ru, Rh, Pd	Usually single phase alloy, sometimes two phase. Some Mo can oxidise to MoO_2 and also form a compound analogous to $Cs_2MoO_4 - (Cs_{1-x}Rb_x)MoO_4$.
Ag, Cd, In, Sn, Sb	Fission yields low; alloyed.

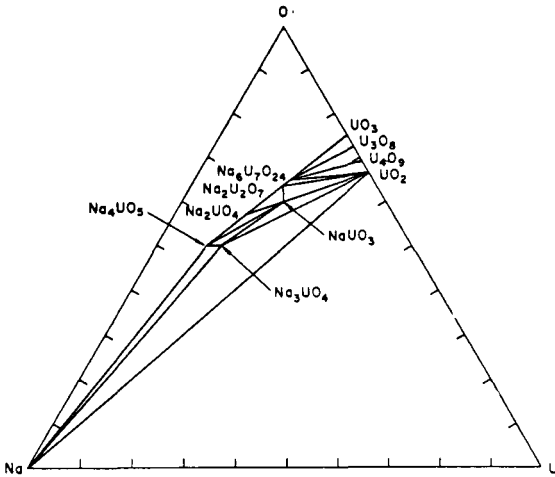


Fig. 8. A section of the Na-U-O phase diagram.

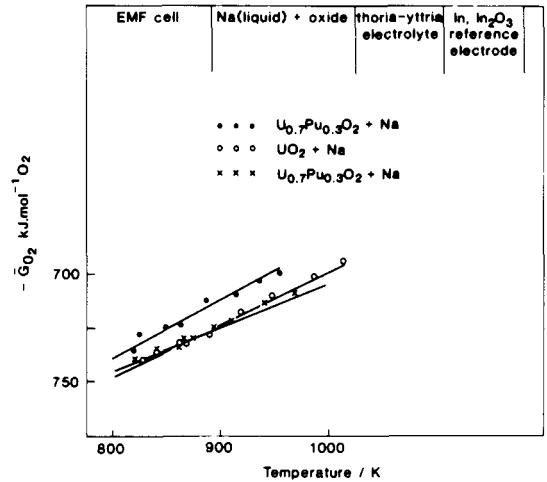
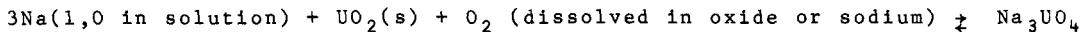


Fig. 9. The experimentally determined variation of \bar{G}_{O_2} with temperature for sodium-urania and sodium-urania-plutonia.

and the equilibrium reaction is



The threshold O:U ratio for the reaction is very close to 2.00 and the threshold oxygen concentration in sodium is 1 wppm at 1073K (ref. 61).

The equilibrium thermodynamic oxygen potential ($\bar{G}_{O_2}^{eq}$) for the reaction is given by

$$\bar{G}_{O_2}^{eq} = \Delta_f G^{\circ}[Na_3UO_4(s)] - \Delta_f G^{\circ}[UO_2(s)] - 3\bar{G}[Na(l)]$$

where $\Delta_f G^{\circ}[Na_3UO_4(s)]$ and $\Delta_f G^{\circ}[UO_2(s)]$ are the Gibbs energies of formation of Na_3UO_4 and UO_2 respectively and $\bar{G}[Na(l)]$ is the partial molar Gibbs

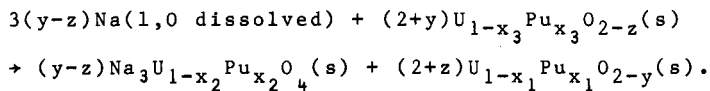
energy of liquid sodium which, because of the small quantities of oxygen present, can be taken as zero. The values for $\bar{G}_{O_2}^{eq}$ were obtained from measurements with an EMF cell; the cell was based² on a thorium-yttria electrolyte and the EMF was measured with a slurry of Na(l), UO_2 and Na_3UO_4 at one electrode and a mixture of In and In_2O_3 as the reference electrode. The oxygen potential can be expressed by

$$\bar{G}_{O_2} \text{ (J.mol}^{-1}O_2) = -949787 + 253.1T$$

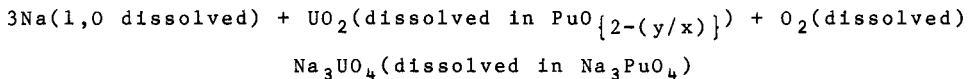
for which the estimated uncertainty, including the error in the value for $\Delta_f G^\circ [In_2O_3(s)]$ is 2.7 kJ.mol⁻¹ O_2 (ref. 62). These data are in good agreement with an earlier determination (ref. 63).

It should be noted that for the reaction between sodium and hyperstoichiometric urania (UO_{2+x}) different mechanisms occur at low and high temperatures. The more destructive reaction between sodium and pellets of urania can possibly be attributed to the formation of the low-density product sodium monoxide (Na_2O) within the grain boundaries at temperatures less than 400°C. As the temperature is raised (450°C) the thermodynamically more stable sodium uranate (Na_3UO_4) is formed. It was also shown that the pellets of stoichiometric urania do not undergo a destructive reaction when in contact with sodium which contains a significant amount of oxygen. A layer of reaction product tends to be loosely held to the surface of the pellet and consists of a high proportion of the phase Na_3UO_4 .

For the urania-plutonia solid solutions the overall reaction can be expressed by



We showed earlier (ref. 61) that when the three condensed phases $U_{1-x_1}Pu_{x_1}O_{2-y}(s)$, $Na_3U_{1-x_2}Pu_{x_2}O_4(s)$ and Na(l) given in the overall reaction above are in equilibrium,² then the equilibrium reactions can be considered in terms of the separate reactions for the uranium and plutonium components of the system. The equilibrium reaction for the uranium component is:



The valency of plutonium in the oxide solid solution is $2[2-(y/x)]$. The oxygen potentials in the phase field of the quaternary system could be expressed in terms of those for the analogous phase field in the ternary system (ref. 61), namely

$$\bar{G}_{O_2}^{eq} \text{ (quaternary system)} = \bar{G}_{O_2}^{eq} \text{ (ternary system)} + RT \ln \frac{a_{Na_3UO_4}}{a_{UO_2}}$$

where $a_{Na_3UO_4}$ and a_{UO_2} are the thermodynamic activities of Na_3UO_4 and UO_2 in the respective solid solutions. It would be expected that, in practice, the values of $\bar{G}_{O_2}^{eq}$ would be almost identical, and our experimental data for the two different compositions of the solid solution and for the urania system (Fig. 9) show this.

Our determinations of the threshold Pu valency from measurements of the lattice parameters of the oxide phase in equilibrium with liquid sodium and sodium uranoplutonate together with measurements of the extent of swelling of oxide pellets on reaction with liquid sodium (ref. 64) indicate that the threshold Pu valency could decrease with increase in temperature of reaction and with increase in Pu concentration. The analysis of these data also indicate that further measurements of the relationship between the composition of urania-plutonia solid solution and its thermodynamic oxygen potential. The dissolution of the fission product cations will influence the extent and rate of the reaction of sodium with irradiated fuel (ref.65).

Analysis of severe accidents in fast breeder reactors

In the introduction we briefly discussed possible severe accidents in a fast breeder reactor. We have examined the loss of flow accident in the proposed British CDFR (ref. 4) and consider the chemical composition of the released fission products with the sodium vapour which forms a rising bubble. When the bubble breaks the surface of the liquid any leak in, for example, the outer seal of the rotating shield would be very small; the condensable species would be those of Cs, Na, I and Te. The role of fission product species in the disassembly of a fast reactor core needs further examination and much attention has been given to examining disassemblies which are driven by the vapour pressure of the fuel. There has been much effort devoted to the prediction and the measurement of thermodynamic quantities for the oxide fuels up to temperatures of 5000K and above. An equation of state (EOS) of the oxide fuel is required which links the important quantities of energy, temperature, pressure and volume. Considerable effort to this end has been expounded (refs. 67-70) using techniques of extrapolation from experimental measurements usually below the liquidus temperature. Although the fuel for a fast reactor is a solution of urania and plutonia, most of the studies on techniques of extrapolation have been carried out on stoichiometric UO_2 . Attempts to predict properties of UO_2 at temperatures greater than the melting point ($3120 \pm 20K$) have stimulated many experimental studies on the liquid, particularly the determination of vapour pressure.

Accurate data for the vapour pressure of fuel are required at temperatures of up to ca. 5000K. Conventional techniques cannot be employed at such high temperatures because of the lack of a material for containment which is compatible with the liquid oxide. Some measurements on the liquid have been carried out using a transpiration technique (ref. 71); in these experiments the containment was tungsten and measurements were made in the temperature range 3175-3390K; at the highest temperature the composition of the liquid at the end of the experiment was $U_{0.94}$. In order to overcome the problems of materials compatibility a number of non-stationary pulse heating techniques have been developed. These dynamic pulse heating techniques require high speed diagnostics and high spatial and temporal resolution. Measurements have been made of vapour pressure up to ca. 5000K using laser beam heating; both Nd-YAG and CO_2 lasers have been employed (refs. 72-77). Recently a heating technique using a CO_2 laser has been employed to measure the boiling point of liquid UO_2 as a function of pressure of an inert gas, xenon (ref. 78). Electron beam heating was employed to determine the relationship between enthalpy and pressure (refs. 79-81). Fission heating has also been used (refs. 82-84). Most of these data are for the vaporization of uranium dioxide, but there are also some data for urania-plutonia solutions. Data have been published for the variation of pressure with temperature in the temperature interval (3700-4090K) (ref. 73), for $U_{0.8}Pu_{0.2}O_{1.96}$ and pressure-enthalpy relationships for $U_{0.77}Pu_{0.23}O_2$ (refs. 80,81).

In order to convert the data for the dependence of pressure on enthalpy to that of pressure on temperature a knowledge of the specific heat (C_p) of the liquid is required. Experimental determinations of the enthalpy content of liquid UO_2 have been made between the melting point (3120K) and 3520K (ref. 85), which gave a constant value for C_p ($135.8 J.K^{-1}.mol^{-1}$). There are estimates of the variation of C_p with temperature which indicate that it could decrease with temperature (refs. 66,83). The relationship used by Breitung and Reil (refs. 83,84) to convert the pressure-enthalpy data was

$$C_p = 149.39 - 5.91 \times 10^{-3} T \text{ J.K}^{-1}.mol^{-1}$$

The vapour pressure data are given for the temperature interval 4800-7500K. Breitung and Reil (refs. 83,84) a best estimate relation for pressure and temperature over the range 3120-8500K give,

$$\log P/\text{Mpa} = 23.7989 \pm 0.1505 - \frac{29605.5}{(T/K)} - 4.7583 \log (T/K)$$

It is suggested (refs. 83,84) that the data obtained using the laser heating technique in which a Nd-YAG laser was used gave slopes which were higher than those of the other data. Ohse et al (ref. 86) indicated that there was a discrepancy between the vapour pressure obtained by using models for the variation of oxygen potential with temperature and those from the measurements using a Nd-YAG laser. The discrepancy between the calculated pressure and measured rate of evaporation into a vacuum is believed to be due to an enhanced rate of evaporation caused by thermionic emission, a process involving surface and space charge effects.

There are several extrapolations of the vapour pressure data into the liquid region using models for the calculation of oxygen potentials for urania and urania-plutonia solid solutions. Ohse et al (ref. 86) give the variation of \bar{G}_{O_2} with temperature for liquid $UO_{2.00}$ based on an extrapolation and assuming equipartition of the enthalpy of fusion between the uranium and oxygen components. The relationship given is

$$\bar{G}_{O_2}(UO_{2.00}, \text{liquid}) / \text{J.mol}^{-1} O_2 = -707000 + 138T(K);$$

no variation of specific heat is included. The partial pressures of all the gaseous species above the system can be calculated using the data for the Gibbs energies of formation of the gaseous species and condensed phase. The total equilibrium vapour pressure is given by

$$\log P_{\text{tot}} / \text{MPa} = -2.717 - \frac{20131}{T(K)} + 1.925 \log T.$$

The predicted vapour pressures are close to those given by the equation representing the experimental data.

A solution to the problem of the apportionment of the enthalpy and entropy of fusion between the partial molal quantities for uranium and oxygen for urania and between uranium-plutonium and oxygen for urania-plutonia solution has been accomplished by Green and Leibowitz (ref. 87). The extrapolation is based on the model for the solid of Blackburn (ref. 88). From these data and the Gibbs energies of the condensed phases and gaseous species, the variation of total pressure with temperature and composition has been derived.

The measured parameters must ideally be fitted to a self consistent set, which forms the equation of state of the nuclear fuel. An excellent survey of the data for the critical point of UO_2 up to 1979 has been compiled by Ohse et al (ref. 89). The methods used to predict these data were the Principle of Corresponding States (ref. 90), the Law of Rectilinear Diameters (refs. 91,92), the Theory of Significant Structures (ref. 93) and a Perturbed Hard Sphere Model (ref. 70). A detailed comparison of the application of these approaches to the prediction of the critical constants and the formation of equations of state has been described by Browning et al (ref. 66). Fischer (ref. 67) has recently included the treatment of non-congruent evaporation into a model using Significant Structures Theory; the predicted critical temperature is ca. 10500K, but will depend on the O:U ratio; this temperature is significantly higher than previous assessments. This methodology could be applied to the prediction of the critical parameters of the mixed oxide.

CONCLUSIONS

We have examined and described some of the information concerning the high temperature thermodynamic properties and phase equilibria which are required for the analysis of design basis faults and severe accidents in nuclear reactors and the prediction of their consequences. Examples are taken from both pressurised water and fast breeder nuclear reactors.

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