MASTER

280
2/16
25 up to CFSTI

uc 80 1221

A Review of the Current Status of Research on the
Chemical and Physical Aspects of Liquid-Metal-Cooled
Fast Breeder Reactor Safety. I. Fission Product
Behavior in Sodium.*[‡]

A. W. Castleman, Jr.
Brookhaven National Laboratory
Upton, New York 11973

ABSTRACT

This is the first of two review papers dealing with the current status of research on the chemical and physical aspects of liquid-metal-cooled fast breeder reactor safety. It summarizes present knowledge on the behavior of fission products comprising the noble gases, halogens, alkali metals, alkaline earth metals, and rare earths, in sodium systems. Considerable information is available on their behavior in the event of minor accidents in which deposition within the reactor primary system and vaporization to the cover-gas would be of concern to the reactor operator. Data on the factors controlling their chemical states and rates of vaporization are discussed. The thermodynamic data available for many of the fission product-sodium systems are shown to be useful in estimating fission

* This work was performed under the auspices of the
U. S. Atomic Energy Commission.

[‡] Prepared for publication in Nuclear Safety.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

product partial pressures above liquid sodium and the maximum extent of vaporization under conditions such that sodium vaporization is significant.

The second paper will review the present status of research on the behavior of aerosols which would be formed in the unlikely event of a catastrophic accident. The nature and behavior of aerosols of PuO_2 , UO_2 , and sodium have a direct bearing on reactor siting criteria and on the design of engineered safeguard devices used to mitigate the consequences of such an accident.

A Review of the Current Status of Research on the
Chemical and Physical Aspects of Liquid-Metal-Cooled
Fast Breeder Reactor Safety. I. Fission Product
Behavior in Sodium.

A. W. Castleman, Jr.
Brookhaven National Laboratory
Upton, New York 11973

The rapid development of liquid-metal-cooled fast breeder reactors (LMFBR's) as a major future power-source raises numerous technical questions related to reactor safety which must be answered before LMFBR's are used extensively. Safety considerations play a large role not only in the overall design and operation of a reactor but also in the development of realistic siting criteria and in the design of engineered safety devices used to mitigate consequences of an unexpected accident. This is particularly true for sodium-cooled fast reactors, which contain large inventories of radioactive fission products, sodium, and plutonium, since the possible distribution of these into the environment presents a major hazard.

During reactor operation, fission products may enter the sodium coolant by several processes, which may be independent or in some cases simultaneous. These include fission product release from fuels by diffusion through cladding or penetration through cladding defects, and entrance by intentional venting

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

of a fuel element. The possibility of fission product deposition and buildup on reactor surfaces such as piping, heat exchangers, pumps, and free surfaces above the coolant, as well as their collection in cold-traps used for sodium purification, is of direct concern in both reactor design and operation. The behavior of fission products possibly released through leaks in reactor off-gas lines, or during fuel element handling and reactor maintenance operations is also important. Finally, because of the existing and proper USAEC philosophy of ensuring public safety, overly conservative licensing regulations will be imposed on reactor designers and utility companies unless detailed technical information is available on the possible consequences of a power reactor accident. These directly influence the selection of reactor containment and of sites for reactor location.

The Reactor Safety Branch of the USAEC is sponsoring a safety program formulated under contract with the LMFBR Program Office at Argonne National Laboratory.⁽¹⁾ As part of a comprehensive program dealing with all important aspects of LMFBR safety, a well balanced research effort is under way to obtain both useful basic data and practical results from engineering tests in order to determine the chemical and physical behavior of fission products and nuclear materials under the wide

variety of conditions that would be encountered in the unlikely event of an accident.

Similar work is being done in Belgium, France, Germany, Great Britain, and the Netherlands. The work in Belgium and France has been primarily on the behavior of fission products released from fuels into sodium and subsequently vaporized under both inert conditions and those expected with a sodium fire. The British work also has been concerned largely with fission product behavior. The Germans, and more recently the Dutch, have concentrated on the behavior of the aerosols of nuclear materials, and the Japanese are initiating similar research.

About two years ago, Keilholtz and Battle⁽²⁾ reviewed fission product release and transport in liquid-metal-cooled fast breeder reactors. They discussed fission product and aerosol work and also fuel element design, fission product distribution in fuel, the types of studies under way at specific laboratories around the world, and the impetus which led to this work. This information need not be repeated here.

The present paper is the first of two reviewing the chemical and physical aspects of LMFBR safety. It summarizes our present knowledge of sodium systems. The behavior of each class of fission products is emphasized rather than the data

obtained by each research laboratory. A complete survey of fission product behavior in sodium necessarily repeats some material contained in the earlier review, but no effort has been made to refer to every available publication.

The second paper, to appear in the next issue of this Journal, will deal with the behavior of the aerosols of PuO_2 , UO_2 , and sodium. Both experimental data and the results of theoretical work as they apply to LMFBR safety will be discussed. Considerable progress has been made in the latter area since the earlier review.

Fission Product Behavior

Fission products come from virtually every group of the periodic table, but considerations of yield, radioactive decay properties, biological hazards, and volatility, limit those of major importance in reactor safety to only a few classes. These include the noble gases, halogens, alkali metals, alkaline earths, and to a lesser extent the rare earths.

In water reactors, iodine (halogen) received the most attention because of the biological hazard associated with ^{131}I (half-life 8.05 days), its volatility, and its reactivity, which often led to the formation of different volatile compounds depending on the chemical environment. Several of these species proved difficult to remove from the gas phase with conventional

traps. Studies of iodine behavior also dominated much of the early work on fission product behavior in sodium systems, although, because of its chemical state in sodium, its behavior is probably less important in these systems than that of cesium (alkali metal) and strontium (rare earth). Although strontium is relatively nonvolatile, its extreme biological hazard and the possibility of its distribution in an aerosol make it much more important than might have been anticipated.

Considerable information has been collected over the years on the extent of release of various fission products, from reactor fuels, including UO_2 , but little is known about their chemical states. Furthermore, the percentage release values are probably not directly applicable to calculations for the types of accidents postulated for the LMFBR's. For the 80% UO_2 -20% PuO_2 fuels to be used in these fast reactors, little specific information is yet available on fission product behavior, although studies are in progress⁽³⁾ and results should be appearing soon. Consequently, although the states of the fission products influence their subsequent behavior in sodium, this review is limited mainly to their behavior directly in sodium, for which data are available. As further information is gained on the states of fission products released from fuels, predictions about their behavior may require some modification.

Noble Gases

The behavior of the noble gases Xe and Kr is of interest because of their relatively small affinity for sodium and their high degree of volatility in these systems. Xe is a precursor of cesium, and Kr of Rb; both daughter products are relatively volatile alkali metals. At high burnup, within totally canned fuel elements, the gases cause large internal pressures. In the case of vented fuel elements, provision must be made for their removal from off-gas systems.⁽⁴⁾

Information on the fate of the noble gases has been obtained from several sources. Both analytical and experimental studies^(4,5) have shown that the design of vented fuel elements can be modified to delay fission gas transfer and thereby substantially reduce the entrance of all but the relatively long-lived species into the coolant. In other studies, the BR-5 fast reactor,⁽⁶⁾ containing some failed $\text{PuO}_2\text{-UO}_2$ fuel elements, was operated to a burnup level of 6.5%, and, as expected, substantial quantities of the isotopes of Xe and Kr were found to have been released into the cover gas. Similar observations were made after the accidental release of fission products from the SRE⁽⁷⁾ and the Fermi Reactor,^(8,9) and from a failed experimental capsule in the EBR-II.⁽¹⁰⁾

Saroul^(11,12) did experiments in two facilities, Pirana and Atena, in which he melted uranium containing the noble gases and in some cases injected higher concentrations of these gases. The results suggested that rare gas retention in liquid sodium is not negligible. However, since a satisfactory material balance was not obtained in either facility, it is questionable whether the rare gases were actually retained in the sodium to a significant extent or whether in fact they ended up in free spaces not readily accessible for analysis.

Data on the solubility of Kr (and Ar) in liquid sodium as a function of temperature,^(13,14) as expected, follow Henry's law; the quantity dissolved in the liquid phase is directly proportional to the partial pressure in the gas phase. Since the proportionality constants (Henry's law constants) are quite small, even in the case of large sodium and fission gas inventories, the noble gas solubilities are predicted to be negligible,⁽¹⁵⁾ except possibly in the sodium thermal bond in a totally canned fuel element.

Halogens

Both iodine and bromine are fission product halogens, but because of the low fission yields and short half-lives of bromine isotopes only fission product iodine is important with respect to reactor safety. Tests at General Electric⁽⁵⁾ on

vented fuel elements showed the release of iodine to the coolant to be near the limit of detection. This indicated that the iodine was retained inside the fuel can, although the presence of traces of sodium at the top of the blanket may have been partly responsible for the low quantity of material transferred. The results in the BR-5, ⁽⁶⁾ SRE, ^(7,16) Fermi, ^(8,9) and EBR-II ⁽¹⁰⁾ incidents showed that most of the iodine released from fuel is retained in the liquid sodium.

To study the transport and plateout of fission product iodine released from U, experiments were done in the Pirana and Atena test facilities ^(11,12) in which uranium was melted and fission products were released into a sodium pool over which an argon sweep was maintained. The iodine that entered the gas phase was found associated with condensates of sodium vapors; the absence of detectable amounts of any other fission products suggested that the iodine was in the form of sodium iodide. Some distribution ratios between the liquid and gaseous phases have been published, but, since it is doubtful that equilibrium had been obtained, the values have no quantitative significance without accompanying rate data. However, the results do show that most of the iodine is retained in the sodium, with a large fraction concentrated near the gas-liquid phase boundary rather than homogeneously distributed throughout

the bulk liquid. Significant quantities of the iodine were removed when the vessels were drained after the experiments, but appreciable quantities remained on surfaces covered by sodium films. Simple decontamination procedures that took off the sodium without disturbing the wall surface were sufficient to remove most of the iodine. The iodine concentration in a sodium deposit of 0.5 mm average thickness was about 300 times that in the liquid sodium in the tank. It was concluded that the iodine had not penetrated into the walls.

In studies at Belgonucleaire, ⁽¹⁷⁾ UO_2 was melted and then contacted simultaneously with sodium and air at 50% relative humidity in a closed vessel. The time dependence of the fraction of the iodine remaining airborne was measured. Following this, the experiments were repeated, but without sodium. A comparison of the results of the two sets of experiments showed that the presence of sodium resulted in the formation of sodium oxide particles which apparently captured the fission products and kept them suspended in the gaseous phase, thus hindering their removal by deposition on the wall. Whether the presence of particles will lead, in general, to prolonged airborne fission product concentrations depends on vessel geometry.

Saroul ⁽¹²⁾ has reported preliminary results of experiments in which sodium containing ^{131}I was burned and the resulting

aerosol was sampled with the use of both an asbestos filter and an activated charcoal trap. The finding of essentially no iodine on the charcoal suggested that the iodine either was retained by the aerosol and/or remained in the chemically combined state NaI rather than dissociating to molecular iodine. This is in agreement with some preliminary results of Castleman and Tang,⁽¹⁸⁾ who found that NaI did not oxidize to yield free iodine in the presence of an excess of sodium oxide. Calculations made with available free energy data for the reaction

showed that dissociation to I_2 should be minimal at the partial pressures of oxygen in the air and in the presence of an excess of Na_2O which fixes the activity of Na_2O at unity.

It is particularly important to know whether fission product iodine is likely to be chemically combined only with sodium or also with other fission products. The large-scale studies reviewed above indicated that the iodine was present only as NaI. Theoretical studies,⁽¹⁹⁾ based on thermodynamic calculations and estimates of fission product yields, suggested that, if iodine were to react with other fission products, cesium was the most likely. However, estimates of chemical activities

from appropriate phase diagrams suggested that even the formation of this inter-fission product compound was unlikely for the low concentrations present and at the temperatures, higher than several hundred degrees centigrade, expected in a reactor system. To verify this, Castleman, Tang, and Mackay⁽¹⁹⁾ did a number of experiments which showed that CsI readily decomposes in the presence of excess sodium to form NaI and elemental cesium.

Castleman and Tang⁽²⁰⁾ did additional experiments to ascertain the activity coefficient of NaI in sodium, which is directly related to the iodine (as NaI) partial pressure over a sodium coolant. If the activity coefficient is known, the maximum extent of fission product release can be calculated (by a method discussed in a later section). The partial pressure of a fission product, P_i , is related to the vapor pressure of the pure compound, P_i^O , and to its activity coefficient, γ_i , and mole fraction, X_i , through the expression

$$P_i = P_i^O X_i \gamma_i$$

Here,

$$\gamma_i = \exp \Delta \bar{F}^E / RT$$

and

$$\Delta \bar{F}^E = \Delta H - T \Delta \bar{S}^E$$

where

$\Delta \bar{F}^E$ is the excess free energy of mixing, ΔH is the heat of mixing, and $\Delta \bar{S}^E$ is the excess entropy of mixing.

For dilute solutions of NaI in sodium, this leads to

$$P_{\text{NaI}} = P_{\text{NaI}}^{\circ} X_{\text{NaI}} \exp \left(\frac{15,900 - 6.8 T}{RT} \right)$$

where T is expressed in $^{\circ}\text{K}$. Work done independently by Clough⁽²¹⁾ is in good agreement. On the basis of this work, little iodine is expected to be present in the vapor phase above the sodium coolant of a fast reactor in the absence of significant vaporization of the sodium. This agrees with observations both in the engineering scale tests and in the several reactor incidents for which data are available.

Alkali Metals

Because of the volatility of metallic cesium and the long half-life (30 yr) and relatively high fission yield of ^{137}Cs , the behavior of cesium is of particular interest. Fission product rubidium, also an alkali metal, is also of some interest, but its behavior has far less relevance to reactor safety.

The data from the BR-5 reactor operated with some failed fuel elements showed substantial levels of radioactivity due to ^{137}Cs . When the plutonium burnup in the fuel elements exceeded 3%, ^{137}Cs was detected in coolant samples; the activity

was 20% that of the ^{22}Na isotope. ^{136}Cs activity in the coolant and on the walls of the circuit was appreciable only when there were large leaks in the fuel elements. The cold-trap designed to purify the sodium of oxides, when connected to the circuit, was found to trap 90% of the cesium activity. After shutdown, most of the ^{137}Cs deposited on the walls of the cooling system and in cold-traps after the external electric heating of the cooling system was shut off. (22)

Monitoring of the behavior of cesium, following a fuel cladding failure incident in the SRE, (7,16) showed, after correction for decay, that ^{134}Cs and ^{137}Cs were decreasing at the same exponential rate, which suggested removal by physical or chemical processes dependent on the state of the element. However, information on fission product behavior obtained from this incident should be viewed with reservations because the failure was caused by the presence of large quantities of carbonaceous materials in the coolant which may have acted as a fission product "getter."

The behavior of fission products released from a Pu (34 wt %) Co-Ce alloy (irradiated to 10^{19} fission and cooled for 2 to 3 yr) into a flowing stream of sodium has been reported by Clifford, et al. (23,24) The cesium was found to be relatively mobile, being both volatile and weakly adsorbed on

stainless steel surfaces in the 300^o to 600^oC range. After 145 hr of circulation, 57% of the cesium was found to have migrated to the gas space above the sodium and 12% was found on stainless steel mesh adsorption test surfaces located in the flowing stream. The other 31% was either in the hot-traps or in the stainless steel tubing; about a third of this was apparently dissolved in the sodium. The distribution between the loop system and the gas phase was reversible: most of the cesium deposited on the stainless steel mesh surfaces when the loop was maintained at 200^oC, but at sodium temperatures between 350^o and 500^oC most migrated to the gas phase. The insertion of graphite into the loop reduced the cesium concentration in the gas phase and on the loop walls after circulation had continued for long periods. Clifford, et al. confirmed this cesium behavior in some capsule experiments. Their findings suggest that cesium is in the elemental form, is only weakly adsorbed on metal surfaces, and readily migrates to gas spaces.

They also investigated the collection and retention of cesium in sodium oxide cold-traps. (23,24) These traps remove substantial quantities of cesium from sodium, but the activity apparently was not fixed, since small changes in temperature resulted in 10 to 20% changes in total cesium content.

Zwetzig⁽¹⁶⁾ also has reported experiments on the behavior of fission product cesium in sodium, particularly upon circulation through cold-traps used for sodium oxide removal. His purpose was to investigate the apparent high efficiency of cold-traps for removing cesium from the sodium coolant as observed in the SRE. One postulated removal mechanism was adsorption of cesium on deposited sodium oxide. However, the reported data show cesium deposition with decreasing temperature even before the limits of oxide solubility are reached. Cesium deposition apparently does not depend exclusively on the presence of precipitated Na_2O , though it is enhanced somewhat by increased oxide concentration.

Saroul^(11,12) has studied the behavior of cesium released into the Pirana vessel and the Atena loop. Some recent Pirana experiments were done in a 250-liter vessel containing 120 liters of sodium; unfortunately, the oxygen content was not controlled. A marked enrichment of cesium in the vapor phase was found by a factor ≈ 10 to 20 times as great as that for iodine enrichment. In one experiment at 550°C , the quantity of cesium per gram of sodium in the vapor was 9.9 times that in the liquid, but on a volume basis the ratio was 6×10^{-5} .

The distribution of the cesium was found to be essentially homogeneous except directly adjacent to surfaces. Somewhat

higher concentrations were found at the gas-liquid surface than below the liquid level. When the vessel was drained, appreciable cesium was found at the surface. About 2/3 of the cesium that was not removed with the sodium was in the sodium film adhering to the walls, and almost 1/3 had penetrated the vessel wall to a depth of 2 to 4 microns.

Meyer, et al.⁽²⁵⁾ reported that in the EBR-II the concentration of trace elements such as cesium exhibited inhomogeneity at a surface. For example, the cesium content of an extruded sample of EBR-II sodium was less than that of sodium remaining in the extruder by several orders of magnitude. They found that in solid samples cesium was concentrated at all surfaces, both metal-wall and metal-gas. They considered the possibility that wall adsorption was responsible for the observed cesium behavior but rejected it on the basis that cesium was found not only at the metal-wall interface but also at the metal-gas interface. Ebersole, et al.⁽²⁶⁾ remelted sodium samples containing cesium, poured the sodium out of the vessel, and observed no major loss of cesium to the container wall.

Castleman, Tang, and Mackay,⁽¹⁹⁾ in experiments discussed above in relation to halogens, showed that, at fission product concentrations expected in reactors, cesium would exist in the elemental state rather than in chemical combination with another

fission product. Analytical and experimental work^(19,20) have been done to deduce the thermodynamic properties of cesium-sodium solutions, and from these extents of vaporization and partial pressures can be calculated. Reliable thermodynamic values are now available⁽²⁰⁾ for the entire range of cesium concentrations from 0 to 100 mole percent.

Studies on the rate of cesium transport by the same authors^(20,27) showed that release from liquid sodium to a gaseous phase (inert gas) is controlled by diffusion rates in both phases, and for well defined flow conditions these rates can be predicted quite accurately. The measured maximum extent of vaporization was in good agreement with predictions from the thermodynamic values. These calculations are discussed in a later section.

A very limited amount of work has been done on the behavior of fission products released during a sodium fire. As part of the FANAL program, Saroul⁽¹²⁾ is testing this in a 25-m³ chamber. In one preliminary experiment in a 400-liter chamber, 10 times as much cesium as iodine was found to be transported along with the sodium oxide aerosol, although the initial concentrations of the two in the liquid phase were about equal.

Descamps, et al.⁽¹⁷⁾ have made preliminary studies of the behavior of cesium after release from UO_2 and subsequent

contact with sodium and oxygen. Like the iodine results measured in the same experiment, the cesium results showed retention in the gaseous phase to be significantly prolonged in the presence of the aerosol compared with release directly into air.

The behavior of fission product rubidium has received very little attention, particularly in large-scale systems. Employing methods similar to those used in the cesium-sodium work, Castleman and Tang⁽²⁰⁾ have also calculated the appropriate thermodynamic properties for the rubidium-sodium system. Since these were omitted from the Proceedings, they are given here (Table I).

The fission products cesium and rubidium are expected to behave in a similar manner. Both are quite volatile compared with sodium, and, depending on the relative proportion of vapor and liquid phases, would be expected to distribute between the two in significant amounts. The unexpected observation that cesium is concentrated near free surfaces requires further study to ascertain the conditions under which this occurs and to determine the reasons for it.

Alkaline Earth Metals

Fission products Ba and Sr are alkaline earths. Since Sr is biologically extremely hazardous, its behavior in reactor systems is of particular concern.

Because of their relatively nonvolatility, the alkaline earth metals have generally not been observed to be directly transported from a fuel element into sodium in vented fuel element tests.⁽⁵⁾ Clifford, et al.⁽²³⁾ observed the behavior of strontium in some small-scale loop tests in which sodium was flowing over a Pu-Co-Ce fuel alloy. Sr collected on the stainless steel and zirconium surfaces of a cold-trap (maintained at 300° to 500°C) and a hot-trap (>500°C). The strontium collection on the low temperature section was greater by more than an order of magnitude than that on the high temperature section. Slightly more strontium was found per unit area on the stainless steel than on the zirconium surfaces.

Limited observations on the behavior of Sr^{89} and Sr^{90} were made following a fuel element failure in the SRE.⁽¹⁶⁾ As with cesium and cerium, the two strontium isotopes were observed to have nearly the same depletion factor, which suggested removal processes dependent on the state of the element.

Saroul⁽¹¹⁾ observed the behavior of Ba released from molten uranium into sodium. In all tests, most of the barium was found to deposit on the walls of the Pirana vessel. After an experiment the barium was not removed by dissolving the sodium film adhering to the walls after the vessel was drained. Washing

the surface with a 5% HNO_3 solution removed the barium which indicated that the barium had not penetrated the metal to any appreciable depth as had cesium during similar tests.

Castleman and Tang⁽²⁰⁾ have used existing phase diagrams to estimate the thermodynamic properties (activity coefficients) for elemental strontium and barium dissolved in liquid sodium. An excess free energy of mixing of 2885 cal/mole was calculated for infinitely dilute solutions of strontium in sodium, assuming the solutions to be regular ($\Delta \bar{S}^E = 0$). Because of the uncertainty in the strontium-sodium phase diagram⁽²⁰⁾ and the regular solution assumption required in making the calculation, it is clear that this system requires further investigation.

The excess free energy of mixing for the barium-sodium system was calculated⁽²⁰⁾ from the phase diagram reported by Kanda, et al.⁽²⁸⁾ The estimated $\Delta \bar{F}^E$ value for infinitely low barium concentrations is 1700 cal/mole, again based on the assumption of a regular solution.

Although the chemical states of the other fission products are relatively well established, the states of Sr and Ba in solution are less certain. At high fission product concentrations, Sr and Ba are probably elemental, and the estimated thermodynamic values are useful in predicting their behavior. However, at very low concentrations, the elements likely

interact with the dissolved oxygen present in reactor-grade sodium. Since the nature of even the oxygen species dissolved in sodium is not well known, their interactions with the alkaline earth metals in solution are even less certain. The free energies of mixing are useful in calculating the extent of formation of individual species, but these quantities are unknown for sodium solutions of oxides or hydroxides of Sr and Ba. However, since the vapor pressure of an alkaline earth element is higher than that of the respective oxide or hydroxide, the partial pressures deduced by assuming these fission products to be in the elemental state would be the maximum under practical conditions.

Recently, Clough⁽²⁹⁾ measured the relative vaporization of strontium and sodium in order to determine the probable chemical state of the dissolved strontium and the thermodynamic properties of the system. A distillation apparatus was used to measure the volatility at 500°C. The experimental data were scattered, but they showed the relative vaporization of the strontium to be considerably less than that expected for the element. This finding plus some thermodynamic estimates suggested that, in very low concentrations, both strontium and barium would likely interact with the dissolved oxygen to form some relatively involatile species.

Clough⁽²⁹⁾ found a significant quantity of strontium apparently adsorbed onto the stainless steel surfaces of the distillation vessel, although at least 18% of the strontium was free for vaporization. This led to other studies of strontium adsorption onto surfaces, done by drying strontium salts from aqueous solutions onto stainless steel surfaces and then equilibrating these with liquid sodium for varying lengths of time. The strontium was found to remain largely on the surfaces, only 5 to 10% being removable (depending on Sr concentration) even after long equilibration times. The author postulated⁽²⁹⁾ that strontium is chemisorbed onto the stainless steel and that the amount removed into the sodium depends not on a simple solubility mechanism but on both the total quantity of strontium involved and the condition of the stainless steel surface.

Rare Earths

Cerium and lanthanum are the primary rare earth fission products. Very little is known about their behavior, but they are not volatile and are probably not of great importance to reactor safety. In the General Electric vented fuel tests⁽⁵⁾ the release of cerium into the sodium coolant was below the limit of detection. Nothing has been reported on the behavior of Ce or La in the EBR-II, BR-5, or Fermi incidents, presumably

because of the insignificant release. La should be found along with the alkaline earth metals because it is formed largely from the decay of the parent Ba isotope rather than by direct fission.

Saroul^(11,12) has reported some information on Ce and La. In the release of these fission products from uranium into sodium, 13% of that released was found dissolved in the sodium near the source of release, 84.5% was in the wall deposits, and only 2.5% was in the liquid in the main vessel. Other tests showed similar results. In each case the cerium eventually ended up mainly on the walls of the system.

A pseudo-first-order depletion constant for ^{141}Ce and ^{144}Ce was obtained following a fuel element failure in the SRE.⁽¹⁶⁾ As with cesium, the depletion constants suggested that the removal mechanisms depended on the state of the cerium, but the presence of carbonaceous material indicated similar reservations concerning the validity of the observations.

Descamps, et al.⁽¹⁷⁾ have reported observations on the nature of cerium released from UO_2 at high temperatures followed by contact with sodium and air. The cerium fission product disappeared more rapidly from the atmosphere in the presence of sodium aerosol than in tests without sodium.

Predicting Fission Product Transport and Deposition from Sodium

It has been shown that, in general, the rate of fission product release from sodium is dependent on transport rates in both the liquid and gaseous phases.^(20,27) Of particular interest with respect to reactor safety is the maximum extent of fission product release to be expected in the event of a reactor accident. In the case of maximum release, processes such as thermal convection and turbulence in the liquid phase, leading to a condition of almost complete mixing, will result in the near elimination of transport resistance in the liquid phase. Consequently, a greater release rate will be obtained with mixing than with diffusion alone operating in both phases.

It was recently proved⁽²⁷⁾ that the limiting case of equilibrium vaporization represents the maximum extent of release. The proof was based on appropriate relationships accounting for diffusion in the gaseous phase, with the liquid phase assumed to be almost completely mixed. If the release rate is considered to be controlled by diffusion through a gas film of thickness b , it follows (with approximations) from the solution to Fick's law, with appropriate boundary conditions, that

$$\log_e (1-F_1) = - \frac{D_{v13} P_1^0}{RTb\rho} \frac{t}{l}$$

and

$$\log_e (1-F_2) = - \frac{D_{v23} P_2^0 \gamma_2}{RTb\rho} \frac{t}{l}$$

where the subscripts 1, 2, and 3 refer to sodium, fission product at infinite dilution, and gas phase, respectively. F is the fraction vaporized, P^0 the vapor pressure, D_v the gas phase diffusivity, ρ the molar density, and t the vaporization time, and l the liquid depth.

Dividing the second equation by the first, one obtains

$$\frac{\log_e (1-F_2)}{\log_e (1-F_1)} = \frac{P_2^0 \gamma_2}{P_1^0} \left(\frac{D_{v23}}{D_{v13}} \right) = A\varphi$$

$$F_2 = 1 - (1-F_1)^{A\varphi}$$

When the ratio of the gas phase diffusivities, φ , is unity, this equation reduces to the familiar Rayleigh equation for equilibrium vaporization.⁽³⁰⁾ Since gas phase diffusivities are inversely proportional to the square root of the reduced mass of the system, in fission product-sodium systems the above diffusivity ratio is always less than unity. Therefore, the Rayleigh equation represents an upper limit for the fractional fission product release as a function of the fraction of sodium vaporized. The latter quantity may often be estimated by making a heat balance for the system under consideration. Obviously the activity coefficients have a direct

bearing on the maximum extent of release, as pointed out earlier. Consequently, the fraction of a fission product vaporized as a function of the fraction of sodium vaporized can be calculated if the value of the constant A is known. For any particular fission product, A can be calculated from the vapor pressures and the appropriate thermodynamic data.

For dilute solutions, A is a function of temperature only:

$$A = a \exp(b/T)$$

Values of the constants a and b are given in Table II for Cs, Rb, Sr, NaI, Ba, Te, and Sb.⁽²⁰⁾ The predicted fractions of fission products vaporized are plotted as functions of the fraction of sodium vaporized in Figure 1. (This figure is similar to that given in Ref. 19, but has been revised to include the latest thermodynamic data available.) The fission product partial pressures per mole fraction are plotted against temperature in Figure 2. The values predicted from the available thermodynamic data for each system (solid lines), and the values predicted assuming ideal solution behavior (dashed lines) are shown.

Work is now under way at Atomics International^(16,31) to develop equations for predicting fission product distributions throughout the primary system of an LMFBR. Calculations are done by means of a computer code to determine individual isotope inventories in the fuel, coolant, deposits on system walls,

cold- or hot-traps, and cover-gas spaces. The code has been programmed to consider up to 50 fission product mass chains having up to 5 members per chain, 5 corrosion products, and ^{22}Na and ^{24}Na . In each case, the cross section for each production reaction is weighted by a "typical" LMFBR neutron spectrum having a mean fission energy of 170 keV. The following regions are considered in computing radioisotope inventories: (1) fuel, (2) fuel-rod gas space, (3) coolant, (4) primary-loop surfaces, up to 10 regions, (5) bypass trapping loops, up to 5 in number, and (6) cover-gas volumes, up to 5 in number.

Once fission products have been released from the fuel cladding, the code accounts for the inventory of the various isotopes in other parts of the reactor system for each of the processes listed in Figure 3. This program will make direct use of kinetic and thermodynamic data on fission products in sodium and will also use information on chemical states and adsorption on surfaces obtained in many of the basic laboratory studies and loop tests currently in progress in various laboratories throughout the world.

Conclusions

During reactor operation, fission products continually enter the sodium coolant by diffusion through the cladding,

release from failed fuel elements, or direct venting of the fuel plenum to the coolant; in some cases by all three processes simultaneously. The partial pressures exerted by most of the fission product elements are quite small, and primarily only xenon and krypton are released to the cover gas to any significant extent. Fission product iodine reacts with sodium, and its volatility in LMFBR's is considerably less than in water reactors. Except possibly in a sodium thermal bond within a fuel element, where the concentration could reach a level high enough to cause the appearance of a separate phase, fission product iodine probably remains dissolved in the sodium coolant.

Cesium is the most important alkali metal fission product. It is expected to remain in the elemental state and to be distributed between the liquid sodium and surfaces. Some removal in cold-traps used for sodium purification is inevitable, and this may actually prove useful in removing cesium from the sodium. The anomalous adsorption of cesium on surfaces requires further study. In some experiments, cesium has been observed to penetrate into stainless steel walls.

The behavior of barium and strontium requires further study. These elements have very low volatility and probably interact with oxygen dissolved in reactor grade sodium. Experimental

evidence suggests that these alkaline earth metals probably are largely adsorbed on piping in the primary system so that significant quantities do not remain in the liquid sodium. The rare earths cerium and lanthanum are expected to behave in a similar manner.

Computer codes are currently being developed, and quantitative methods of accounting for fission product deposition at specific locations within a LMFBR primary circuit should be available in the future.

Calculational methods and thermodynamic data are currently available for predicting the maximum extent of fission product vaporization as a function of sodium vaporization in the case of cesium, rubidium, strontium, iodine (as NaI), barium, tellurium, and antimony. The results shown in Figure 1 indicate that appreciable quantities of the fission products can be expected to vaporize in the event of significant sodium vaporization.

References

1. Liquid Metal Fast Breeder Reactor Program Plan, Vol. 10, Safety USAEC Res. & Dev. Report, LMFBR Program Office, Argonne National Lab., August 1968.
2. G. W. Keilholtz and G. C. Battle, Jr., Fission-Product Release and Transport in Liquid-Metal-Cooled Fast Breeder Reactors, Nuclear Safety, Vol. 9, 494-509, November-December 1968.
3. Brookhaven National Laboratory, Reactor Safety Program, (in progress).
4. L. Barilli, et al, Fission Product Removal From the Cover Gas of a Vented Fuel FBR, Proceedings International Congress on the Diffusion of Fission Products, Saclay, France, November 1969 (in press).
5. G. L. O'Neill et al., Safety and Economic Aspects of Vented Fuel in Sodium-Cooled Reactors, in Proceedings of the Conference on Safety, Fuels, and Core Design in Large Fast Power Reactors, October 11-14, 1965, USAEC Report ANL-7120(CONF-651009), pp. 540-548, Argonne National Laboratory, 1965, and
G. L. O'Neill, J. H. Davies, and M. L. Johnson, Demonstration of Fission-Gas Venting from Fast Oxide Reactor Fuel Elements, Trans. Amer. Nucl. Soc., 7(1): 92-93 (June 1964).

6. V. V. Orlov et al., Some Problems of Safe Operation of the BR-5 Plant, Proceedings of the International Conference on the Safety of Fast Reactors, Aix-en-Provence, Section VA, Paper No. 7, September 1967.
7. W. B. McDonald and J. H. DeVan, Sodium Reactor Experiment Incident, Nucl. Safety, 1(3): 73-75 (March 1960).
8. A. E. Klickman and R. C. Callen, Anomalous Reactivity Effects in the Fermi Incident, Transactions of the American Nuclear Society, 10, 334, June 1967.
9. October 5, 1966 Fuel Damage Incident at the Enrico Fermi Atomic Power Plant, Status as of February 24, 1967, Atomic Power Development Associates, Inc. Power Reactor Development Company.
10. R. R. Smith, C. B. Doe, and F. S. Kirn, The Application of Cover-Gas Monitoring in the Recent EBR-II Fission-Product Release, Trans. Amer. Nucl. Soc., 10(2): 634 (November 1967), and
E. R. Ebersole and R. Villarreal, Diagnostic Radiochemistry Following the Recent EBR-II Fission-Product Release, Trans. Amer. Nucl. Soc., 10(2): 634-635 (November 1967) and also see R. R. Smith et al., ANL 7543.
11. J. Saroul, Investigation on the Behavior of Fission Products in Sodium and Argon--PIRANA Experiments, Proc. of International Conf. on the Safety of Fast Reactors, Aix-en-Provence, Section VB, Paper No. 1 (1967).

12. J. Saroul, Out of Pile Studies and Diffusion of the Contamination in Liquid Sodium and Fast Reactor Containment. New Experimental Program. Proceedings International Congress on the Diffusion of Fission Products, Saclay, France, November 1969 (In Press).
13. R. C. Vogel et al., Chemical Engineering Division Semi-Annual Report, January-June 1964, ANL-6900, pp. 125-126, June 1964.
14. R. C. Vogel et al., Chemical Engineering Division Research Highlights, May 1966 - April 1967, ANL 7350, pp. 59-60, April 1967.
15. W. P. Kunkel, Fission Product Distribution in the FFTF Reactor, NAA-SR-MEMO-12313, Atomics International, March 1967.
16. G. B. Zwetzig et al., The Distribution of Fission Products in LMFBR Sodium Systems, Proceedings of the International Conference on Sodium Technology and Fast Reactor Design, ANL-7520, Part I, pp. 527-533, November 1968.
17. C. L. Descamps, et al., Behavior of Several Fission Products in the Atmosphere Surrounding Sodium-Cooled Reactors in the Event of a Major Accident, Proceedings of the International Conference on Sodium Technology and Fast Reactor Design, ANL-7520, Part I, pp. 555-561, November 1968.

18. A. W. Castleman, Jr., and I. N. Tang, Chemical Considerations in Fast Reactor Safety, in Proceedings of the Conference on Safety, Fuels, and Core Design in Large Fast Power Reactors, October 11-14, 1965, USAEC Report ANL-7120(CONF-651009-6) pp. 848-854, Argonne National Laboratory, 1965.
19. A. W. Castleman, Jr., et al., Fission Product Behavior in Sodium Systems, in Alkali-Metal Coolants, pp. 729-742, International Atomic Energy Agency, Vienna, 1967.
20. A. W. Castleman, Jr., and I. N. Tang, Fission Product Vaporization from Sodium Systems, Proceedings of the International Conference on Sodium Technology and Fast Reactor Design, ANL-7520, Part I, pp. 540-548, November 1968.
21. W. S. Clough, J. Nucl. Energy, 23, 495, 1968.
22. Notes on Reactor Safety in the USSR, Nucl. Safety, 7(2): 159-161 (Winter 1965-1966), and
O. I. Leipunskii et al., Five-Year-Operation Experience on Reactor BR-5 (in Russian) in Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1964, Vol. 4, pp. 372-385, United Nations, New York.
23. J. C. Clifford et al., Behavior of Fission Products in Sodium, in Alkali Metal Coolants pp. 759-769, International Atomic Energy Agency, Vienna, 1967.

24. J. C. Clifford, Behavior of Long-Lived Fission Products in Sodium, LA-3737.UC-80, June 1967.
25. R. J. Meyer et al., Trace-Element Behavior in Sodium, Proceedings of the International Conference on Sodium Technology and Fast Reactor Design, ANL-7520, Part I, pp. 291-294, November 1968.
26. See Ref.(3) listed at the end of the above Ref. 25.
27. I. N. Tang, et al., On the Transport of Fission Product Cesium from Sodium, Advances in Chemistry, (In Press).
28. F. A. Kanda, et al., The Barium-Sodium Equilibration System, J. Phys. Chem. 69, 3867-72, 1965.
29. W. S. Clough, The Behavior of Barium and Strontium Fission Products in Liquid Sodium, Proceedings International Congress on the Diffusion of Fission Products, Saclay, France, November 1969 (In Press).
30. See for instance, W. L. McCabe and J. C. Smith, Unit Operations of Chemical Engineering, pp. 675, McGraw-Hill Book Company, Inc. 1956.
31. LMFBR Fission Product Contamination and Control Studies-A Status Report, USAEC Research and Development Report AI-AEC-12687, Atomics International, June 1968. See also above Ref. (16).

Table I

Partial Molar Quantities for Liquid Na-Rb Alloys

X_{Na}	$\Delta \bar{H}_{\text{Na}}$ cal/mole	$\Delta \bar{S}_{\text{Na}}^{\text{E}}$ e.u.	$\Delta \bar{H}_{\text{Rb}}$ cal/mole	$\Delta \bar{S}_{\text{Rb}}^{\text{E}}$ e.u.
0.0	843	-0.37	0	0
0.1	781	0.15	4	-0.02
0.2	699	0.36	18	-0.06
0.3	602	0.37	51	-0.06
0.4	494	0.27	110	0.00
0.5	381	0.14	203	0.10
0.6	290	0.08	315	0.17
0.7	191	0.03	500	0.27
0.8	98	0.00	784	0.37
0.9	27	0.00	1188	0.39
1.0	0	0.00	1722	0.19

Table II

Constants for Calculating the Extent of Fission Product
Vaporization as a Function of the Sodium Vaporized

<u>Fission product</u>	<u>Temperature range,**°K</u>	<u>a</u>	<u>b</u>
Cesium	700-900	0.121	5,073
Rubidium	700-900	0.213	4,184
Strontium	700-1000	5.41	-5,270
Iodine*	700-1200	0.37	-150
Barium	700-1100	1.73	-7,003
Tellurium	725-1100	2.81	-10,150
Antimony	1000-1100	2227	-21,989

*Present as NaI.

**a and b were evaluated employing vapor pressure data within this temperature range, but are not necessarily restricted to this range for practical use.

Fig. 1

Fig. 2

Inventory	Addition Processes	Removal Processes
Coolant (fission products)	Cladding leakage Parent decay Tramp fuel fission Corrosion of plated deposits	Deposition Trapping Decay Vaporization
Surface	Deposition	Decay Corrosion
Trap	Precipitation Adsorption	Decay
Cover gas	Vaporization	Decay
Coolant (corrosion products)	Corrosion of activated structure Activation of corroded structure	Deposition Trapping Decay

Fig. 3. Processes Used in Calculating Inventories