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FISSION-PRODUCT RELEASE DURING ACCIDENTS - AN ACCIDENT MANAGEMENT PERSPECTIVE

LIBÉRATION DE PRODUITS DE FISSION LORS D'ACCIDENTS - UNE PERSPECTIVE DE GESTION D'ACCIDENTS

C.E.L. HUNT, D.S. COX and F.C. IGLESIAS

AECL Research

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AN ACCIDENT MANAGEMENT PERSPECTIVE

by

C.E.L. Hunt, D.S. Cox, F.C. Iglesias*

* Ontario Hydro
  700 University Avenue
  Toronto, Ontario M5G 1X6

EACL RECHERCHE

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RÉSUMÉ

Un des buts lors de la gestion d'un accident de réacteur est de minimiser
la libération des produits de fission radioactifs. La libération dépend
non seulement de la température mais aussi de la pression partielle d'oxy-
gène. Des atmosphères fortement oxydantes, telles que celles produites
lors de l'accident de Chernobyl, ont libéré des éléments semi-volatils
comme le ruthénium contenant des oxydes volatils. À basse température,
l'oxydation de l'UO_2 en U_3O_8 peut entraîner une forte fragmentation du
combustible et la libération de produits de fission non-volatils sous forme
d'aérosols. Dans des conditions moins oxydantes, quand il y a accumulation
d'hydrogène par la réaction entre le zirconium et l'eau, la basse pression
partielle d'oxygène qui en résulte peut réduire grandement ces réactions.
À TMl-2, seuls les gaz nobles et les produits de fission volatils ont été
libérés en quantités importantes. Une connaissance de l'effet de l'atmo-
sphère ainsi que de la température sur la libération des produits de fis-
sion de coeurs de réacteurs endommagés est donc un élément utile, sinon
nécessaire, d'information pour la gestion d'accident.

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ABSTRACT

One of the aims when managing a reactor accident is to minimize the release
of radioactive fission products. Release is dependent not only on the
temperature, but also on the partial pressure of oxygen. Strongly oxidizing
atmospheres, such as those that occurred during the Chernobyl accident,
released semi-volatile elements like ruthenium, which has volatile oxides.
At low temperatures, UO_2 oxidization to U_3O_8 can result in extensive breakup
of the fuel, resulting in the release of non-volatile fission products as
aerosols. Under less oxidizing conditions, when hydrogen accumulates from
the zirconium-water reaction, the resulting low oxygen partial pressure can
significantly reduce these reactions. At TMI-2, only the noble gases and
volatile fission products were released in significant quantities. A
knowledge of the effect of atmosphere as well as temperature on the release
of fission products from damaged reactor cores is therefore a useful, if not
necessary, component of information required for accident management.

* Ontario Hydro
  700 University Avenue
  Toronto, Ontario M5G 1X6

INTRODUCTION

One of the requirements when managing a reactor accident is to minimize the release of radioactive fission products from the fuel, both into the containment, and ultimately to the environment. The first is to minimize the dose to operators and cleanup staff, and the second is to minimize dose to the public. Both of these depend ultimately on the way fission products are released from the fuel.

It has frequently been assumed that the major factor controlling fission-product release kinetics is the temperature. Thus, the first remedial reaction is to bring the reactor temperature down. This may not necessarily be the best strategy. Consideration must be given to how the temperature is reduced, as is shown below by a few examples taken from the TMI-2 and Chernobyl accidents.

At Chernobyl, within about a day after the initial reactor excursion to near 1500°C,[1] the temperature was successfully reduced over most of the core to about 500°C. This occurred as a result of an air flow being established from the bottom of the core.[1] While this reduced the fission-product release in the short term, it paved the way for a large aerosol release about three days later.[2] Dumping of material on top of the core from helicopters, while again helping in the short term, also set the stage for a large subsequent release of fission products.

A large release that occurred on day 4, and the final large release during the temperature excursion from days 7 to 10, was a direct result of providing a highly oxidizing atmosphere to the fuel at what appears to be a very critical temperature for UO_2 oxidation in air, namely 500°C.

At TMI-2 the fuel pins oxidized in steam at high temperature and the upper region of the core was blanketed with hydrogen. Considerable melting of core components occurred due to the formation of eutectic mixtures. A considerable amount of fission products were released into containment, but a large quantity was retained in the melt. Because, unlike Chernobyl, there was containment, and it remained intact, there was insignificant release to the environment.

Data from AECL studies,[2,3,4] confirmed by results from other laboratories,[5] shows that the environment surrounding the UO_2, as expressed by the chemical potential for oxidation, can be as important as the temperature in controlling the release kinetics of fission products.

EXPERIMENTAL DATA

Parameters Controlling Fission-Product Release

Fission products are frequently divided into four general categories: noble gases, volatile elements like iodine and cesium, semi-volatiles, and non-volatiles. Semi-volatiles are elements that have high melting points either

in the elemental or oxide form, but not in both. The non-volatiles have high melting points in both forms. Ruthenium and molybdenum are examples of metals with high melting points. Their oxides, however, have low melting points and hence high vapour pressures, and are easily volatilized. Cerium is the opposite. The metal melts at 799°C, but the oxide melts at about 2600°C. Barium melts at 725°C, its oxide at 1918°C. Zirconium and niobium are both considered to be non-volatiles, because both the metals and the oxides have high melting points. however, even niobium can be released at moderate temperatures under the right conditions, because it has several oxidation states, one of which appears to be volatile.

Temperature is usually considered to be the dominating parameter controlling fission-product release. However, the oxygen potential has a very strong influence on the release rate of noble gases, volatiles, and the semi-volatiles. In the case of semi-volatiles, it can make the difference between a large release or virtually no release. Thus, how a reactor core is cooled after an accident may be as important as the temperature reduction itself. Some elements like strontium, cerium, lanthanum and zirconium have as high an affinity for oxygen as uranium. As a result, they compete within the UO_2 lattice with the uranium for the available oxygen. Other elements will only oxidize when the UO_2 has itself first oxidized to UO_{2+x}. Ruthenium is the most extreme example of this behaviour. The local oxygen potential, which is seen by the fission product ruthenium, must exceed the value which thermodynamically permits formation of a volatile species. This requires an external oxidizing environment, such as air or steam, reacting with the UO_2 to produce UO_{2+x} or U_3O_8, depending on the local temperature and oxygen partial pressure. After the UO_2 becomes sufficiently oxidized, release of the ruthenium in the oxide form is rapid.[3,4]

Figure 1 is an example of the release of iodine, cesium and ruthenium from a sample of UO_2 oxidized in air at 1600°C. Iodine and cesium were released up to about 30%, while the sample was heating up to the test temperature in an argon atmosphere. Air was introduced and as the sample oxidized, the release rate of these two elements accelerated, and then slowed again as oxidation of the UO_2 was completed. At the end of the test, after about two hours, release of cesium and iodine had reached about 80% and was slowly continuing. Ruthenium showed a delay, while the sample was oxidizing, followed by rapid release, which reached 100% within about 20 minutes. Figure 2 contrasts the release of ruthenium and cesium at 1670°C in steam. In the steam atmosphere, ruthenium release was delayed for about one hour compared with the cesium, and then was much slower than in air at a similar temperature. This is a direct reflection of the oxygen partial pressure available in the two atmospheres, the partial pressure in steam being about two orders of magnitude less than that in air at this temperature.

Iodine and cesium releases are also affected by the oxygen potential, as shown by the cesium curve in Figure 1. The acceleration appears to coincide with the oxidation process. Figure 3 shows this more clearly. During the first part of this test at 1400°C the sample oxidized slowly because of a small amount of oxygen contamination in the argon. If this oxidation had continued to equilibrium, the sample would have reached an O/U ratio of 2.08.

Steam was introduced at about 4000 s into the test. Oxidation accelerated and levelled off at the new equilibrium value of 2.18. The release rate of the cesium also accelerated at the same time as the oxidation rate, but levelled out more quickly, possibly because release was almost complete.

Figure 4 shows xenon and iodine release from fuel oxidized in air at low temperature, 500°C. At this temperature the sample was completely converted to U_3O_8. Release of both elements was low. A stepwise increase in temperature, to 800°C, 1000°C and finally to 1100°C resulted in a similar stepwise increase in the fractional release of these two elements. The release rate dropped almost to zero during the dwell time, possibly because these temperatures are too low for temperature-activated release mechanisms, like diffusion. In an air atmosphere, at these temperatures, the total release appears to be controlled primarily by the final temperature reached. The percentage of the inventory released is much greater than would be the case from unoxidized UO_2.

A temperature of 500°C is significant because, at this temperature in air, UO_2 oxidation is particularly rapid. Figure 5 shows the process schematically. Oxygen rapidly penetrates the grain boundaries, converting them to U_3O_8, which occupies about 30% more volume than the parent UO_2. The boundaries split and the grains separate from the matrix. They can then be attacked from all sides, continue to oxidize and fragment further. The final particle size can be small enough that the particles become airborne as fine aerosols. Figure 6 shows an example of a grain in the process of breaking up.

At higher temperatures fragmentation is less severe, partly because oxidation proceeds more as a front moving through the sample and partly because the U_3O_8 becomes less brittle. However, as shown by Figure 7, a new problem can arise.

In oxidation tests in both air and steam at high temperatures, the sample first gains weight as it absorbs oxygen, and then loses weight at longer times. We have observed this at temperatures above about 1200°C. The cause is the formation of UO_3, which is a gas under these conditions. Figure 8 shows a photomicrograph of the edge of a UO_2 sample exposed in air at 1900°C. If we assume the bulk of the fission products are distributed throughout the fuel, whether they are in solution or as fine precipitates, it is easy to imagine that under these conditions they will all be released. Even if they are not volatile, they will be released as aerosols.

Thus, under highly oxidizing conditions we can release much of the fission-product inventory in the form of aerosols at both low (~500°C) temperatures, and at high temperatures. At intermediate temperatures, oxidizing conditions will only release the volatile and noble gas elements.

EXAMPLES FROM CHERNOBYL

By examining some of the data from the Chernobyl accident we can see in hindsight the impact of some of the actions that were taken on the subsequent release of fission products. This does not mean that the decision-makers necessarily had any other options, even if they had appreciated the potential problems. They were faced with graphite fire, possible burning zirconium alloys and considerable exposed fuel. The obvious actions were to bring down the temperature and to put out the fire. The first was accomplished when a large air flow was established through the reactor. Although this cooled the reactor, it also provided oxygen both for graphite combustion and for UO_2 oxidation. Dousing the fire took longer, and was partly accomplished by smothering the reactor from above with sand, lead and other materials.

Figure 9 shows the published[1] temperature history of the reactor core during the accident. Also included is the activity recorded at Prague, about 1000 km to the east.[6] This data was used because it is one of the more detailed records of the daily fission-product release. The time scales have been adjusted by four days to bring the measurements at Prague into approximate coincidence with events at the site. Only one measurement was made of fission-product release above the reactor between days 1 and 7 (on day 4). As a result, the on-site data shows an almost constant release for the first four days, missing the decrease and subsequent rise again between days 1 and 4, followed by a decrease and then the final peak release corresponding with the reheating event starting on day 7. Coincidence of the last peak with the temperature curve is not exact, probably because of daily variations in atmospheric transport over the intervening 1000 km.

The data shown here and confirmed at other distant monitoring stations shows a marked drop in fission-product release when the reactor temperature first decreased. Unfortunately, the temperature reached was that at which oxidation of UO_2 in air is very rapid, about 500°C, and the oxidation product is a fine powder, typically less than the original UO_2 grain size, as shown in Figures 5 and 6. This set the stage for the increase in fission-product release of almost two orders of magnitude on about day 4, when we believe that these fine U_3O_8 particles became airborne in the high air flow that still existed through the reactor core. The subsequent decrease in fission-product releases from day 4 to about day 6 were most likely the result of smothering the reactor with the many tons of material which was dumped on top of the core. This material no doubt acted partially as a filter, retaining the fine particles of U_3O_8. It also provided thermal insulation, which allowed the temperature to rise again, since graphite was still burning. This temperature rise released fission products trapped in the "filter bed", accounting for the final release, which at the reactor site was as high as the initial release on the day of the accident.[1] At about day 9 the fires were finally put out by substituting nitrogen for the air cooling. If it had been possible to do this at the beginning, the oxidation reactions could have been avoided and the fire would have been doused earlier. The first would probably have avoided the two order of magnitude increase in fission-product release on day 4, and the two together would have avoided the release during the reheating on days 7 to 9.

The release that peaked with the temperature on day 9 was particularly strong for the semi- and non-volatiles. Their release increased by two orders of magnitude over the immediately preceding minimum and by one order of magnitude over either of the two previous peak releases, according to measurements made at the reactor site. This is not apparent from Figure 9, probably because of effects of atmospheric transport. Prague, where the data on Figure 9 was measured, is 1000 km west of the reactor site. The other most complete monitoring station data was from 450 km north.[1] It showed the same sequence of peaks as those at Prague, but the relative magnitudes were slightly different.

EXAMPLES FROM TMI-2

TMI-2 was a vastly different type of accident in terms of core behaviour and fission-product release. There was considerable steam cooling, with the consequent oxidation of the Zircaloy and generation of large quantities of hydrogen. The geometry of the fuel rods was retained throughout the heat-up period, up to the point where the temperature was high enough to start eutectic reactions between them and structural components. Considerable melting of the core occurred and conditions became far less oxidizing for the fuel and the fission products. Fission products like ruthenium remained in the metallic form rather than being converted to the volatile oxide. The only fission products that appear to have been really volatile during this accident were cesium, iodine and the noble gases.[7]

Most of the iodine was probably released in the form of CsI.[8] Only when CsI is subjected to strongly oxidizing conditions does it decompose to Cs_2O and elemental iodine. These conditions would not have occurred until the CsI escaped through the pressurizer and pilot-operated-relief valve to the containment, by which time the temperature would have been sufficiently low to preclude any significant reaction rate.

The release rate of the noble gases and the volatile cesiums and iodines is less sensitive to the oxidation state of the fuel than is ruthenium, temperature being the more dominant factor. Although releases of these elements may have been enhanced by thermal shock breaking the crust on the top of the molten pool and shattering oxidized fuel in the upper region of the core,[8] the majority of the volatile fission-product inventories had probably already been released from the material which formed the molten pool. When the core has reached such a high temperature and water is added, it is hard to visualize how thermal shock can be avoided. If water is introduced slowly, so that it has a chance to vapourize before it reaches fuel surfaces, one runs the risk of providing large quantities of steam, which can oxidize the remaining Zircaloy, increase the system pressure and produce a large additional inventory of hydrogen. In fact, the B circuit pump transient, which introduced some 28 m^3 of water in a very short time,[9] resulted in a significant system pressure excursion[10] and produced a debris bed in the upper region of the core.

The criterion for mitigating fission-product releases under a TMI-2 type of accident, where oxidation is primarily by steam, should be reduction of temperature. Rapid addition of coolant would meet this need. The probability of shock cooling causing the formation of a rubble bed, which may result in an uncoolable geometry, must be considered. Slower cooling, which may prevent rubble bed formation, poses the alternative problem of producing large quantities of hydrogen, a potential large pressure rise, and a potential explosion hazard.

Fission-product release can not be avoided, but the contrast between the releases at Chernobyl compared with those at TMI-2 shows the strong influence of the environment seen by the fuel. In both accidents a major fraction of the core was destroyed. At TMI, with a steam/hydrogen atmosphere, only a very small fraction of the semi- and non-volatile elements was released. These elements were probably released as aerosols and they ended up in the sludge in the basement of the containment building. At Chernobyl, with the highly oxidizing atmosphere, not only were semi-volatile elements like ruthenium released in large quantities, but fine particles of fuel were also produced and released. These carried with them the non-volatiles like barium, cerium, lanthanum, zirconium and niobium. Thus, the importance of a reliable containment building is emphasized. However, if Chernobyl had had a containment building, and if it had not been breached during the accident, there would still have been a contamination problem many times that of TMI to be faced.

SUMMARY

An important difference between the Chernobyl and TMI-2 accidents was that the TMI-2 core was not subjected to strongly oxidizing conditions. The strongly oxidizing conditions prevailing at Chernobyl promoted the release of the volatile fission products, partly by decreasing the stability of CsI in favour of elemental iodine, and caused the disintegration of the fuel and the resultant aerosol formation. The hot, but much less oxidizing conditions at TMI-2, still resulted in release of the volatile fission products, but most of the iodine remained as CsI. By the time the CsI was exposed to oxidizing conditions in the containment building, temperatures were sufficiently low to prevent significant oxidation to elemental iodine. Although fuel melted at TMI-2, most of the refractory fission products remained in solution in the melt. Those that were released as aerosols were precipitated as a result of the moist conditions prevailing in the containment.

It has been shown that temperature is not the only factor to control the release of fission products during a reactor accident. The availability of oxygen, whether from steam or from atmospheric air, can be equally important. It can control the release rate of many fission products. Both the oxidation rate and the form of the oxidized product of UO_2 is controlled by a combination of these two parameters; temperature and $p(O_2)$. During an accident, both must be managed, and the Accident manager must know the consequences of both parameters on the fuel behaviour, fission-product release and transport.

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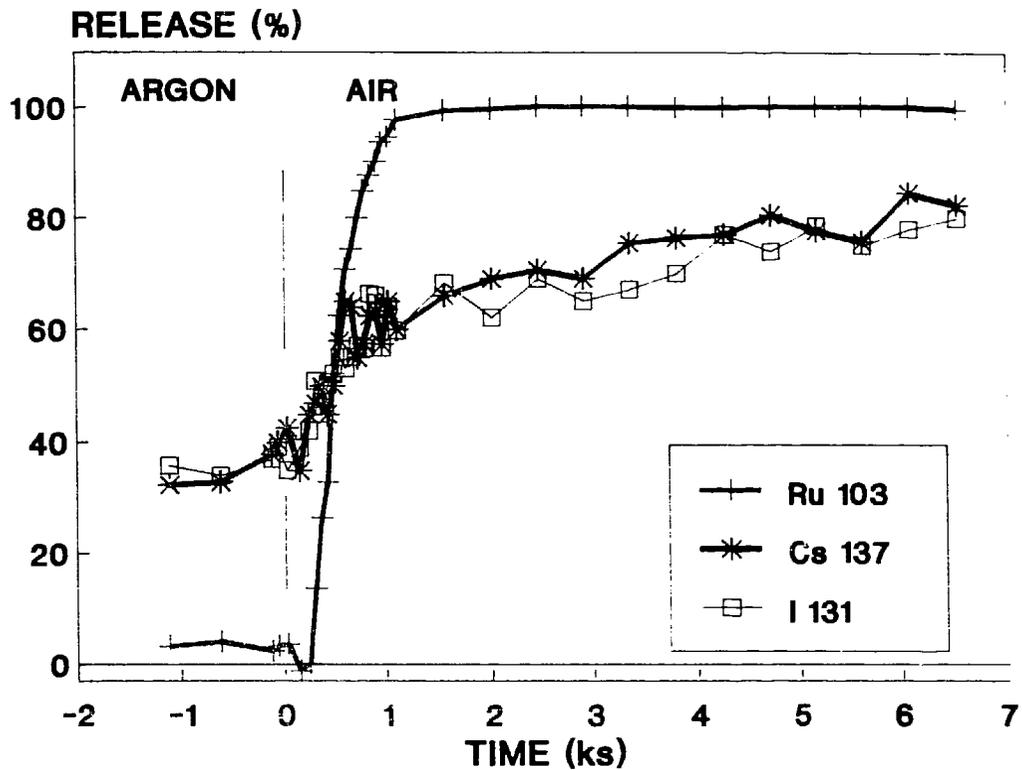
RELEASE (%)

ARGON AIR

FIGURE 1   Release of Ru, Cs and I from UO_2 at 1600°C in air.
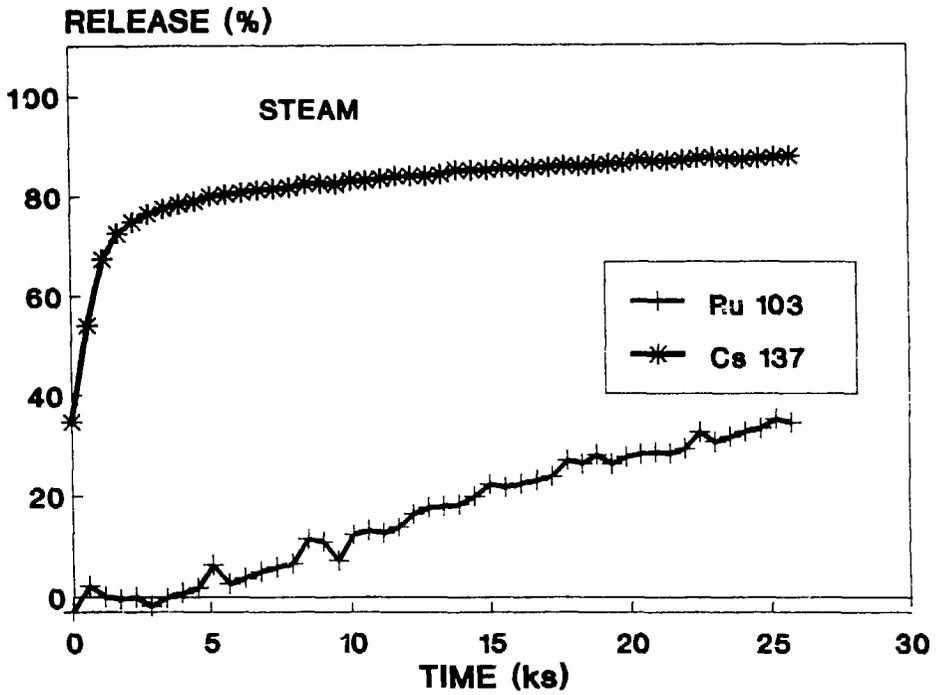
RELEASE (%)

FIGURE 2   Release of Ru and Cs from UO_2 in steam at 1670°C.
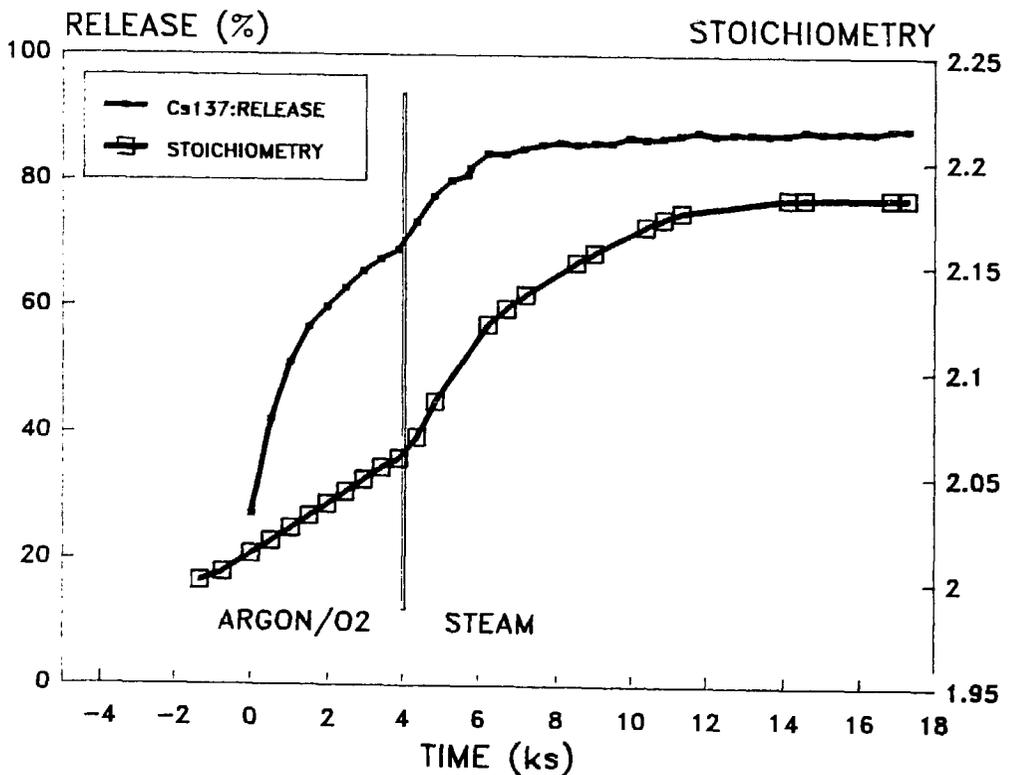
FIGURE 3   Release of cesium with changing stoichiometry at 1400°C.

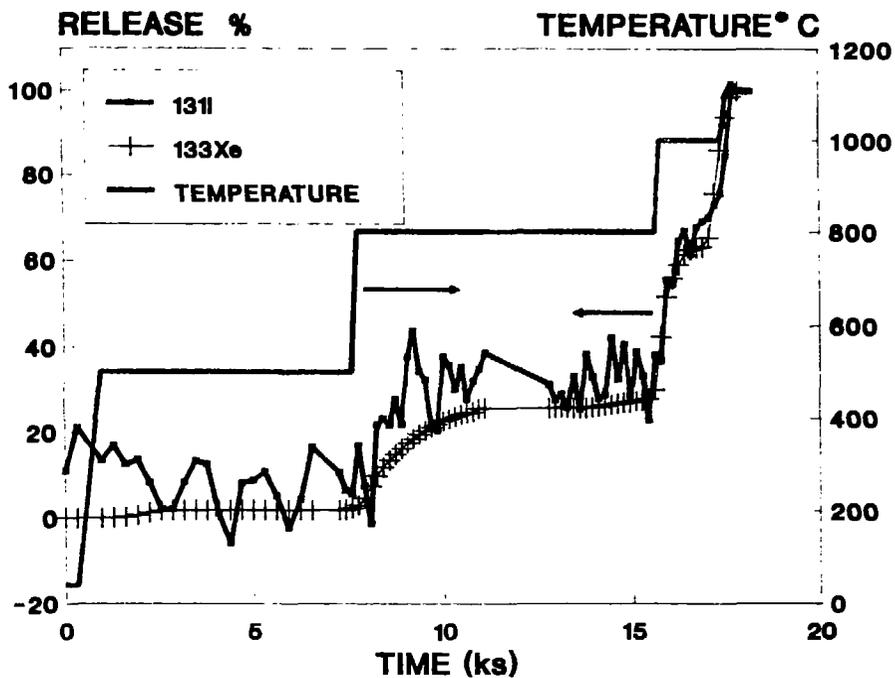RELEASE %   TEMPERATURE° C

FIGURE 4   Release of xenon and iodine from UO_2 ramped in temperature in air.
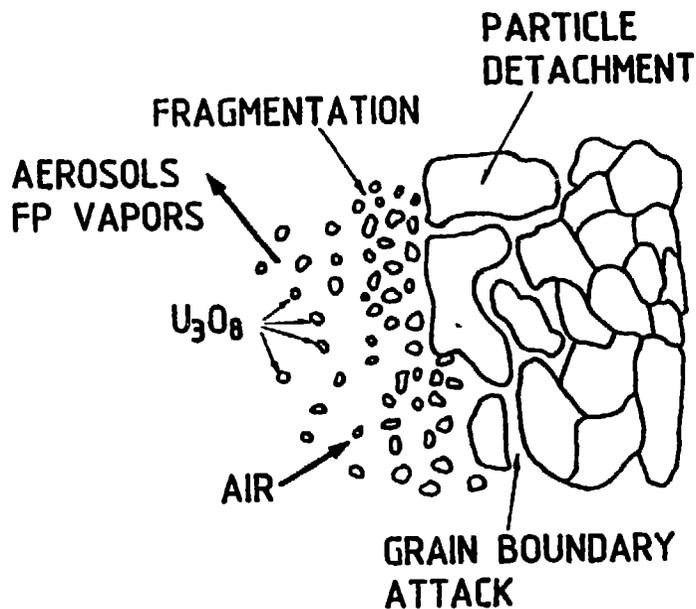
FIGURE 5 UO_2 oxidation in air at 500°C.
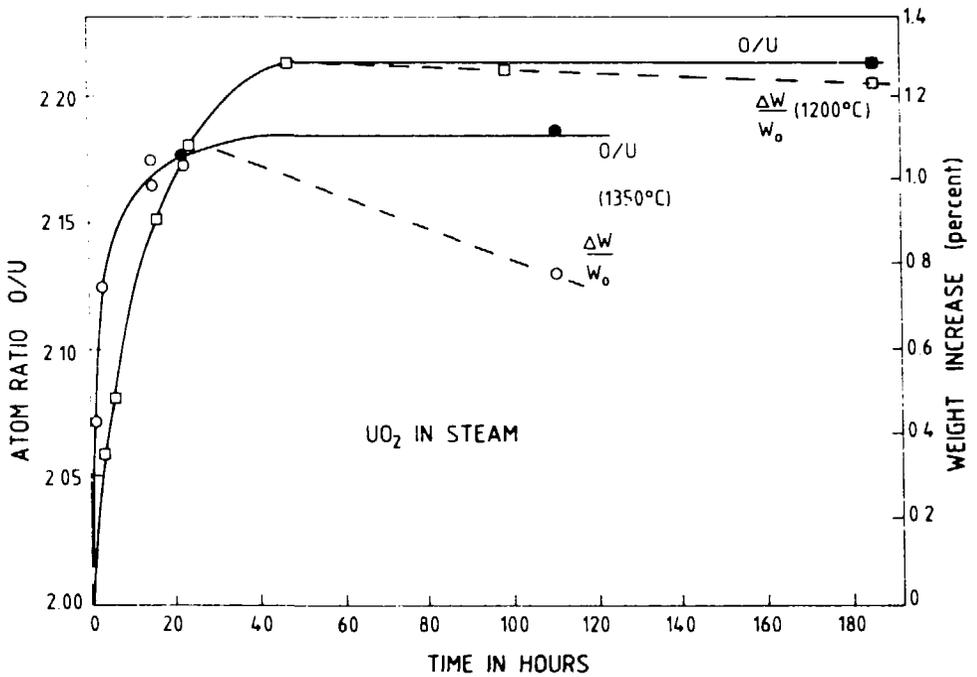
FIGURE 6 UO_2 grain oxidized at 500°C to U_3O_8.

FIGURE 7   Weight loss from oxidizing UO_2 at high temperatures.
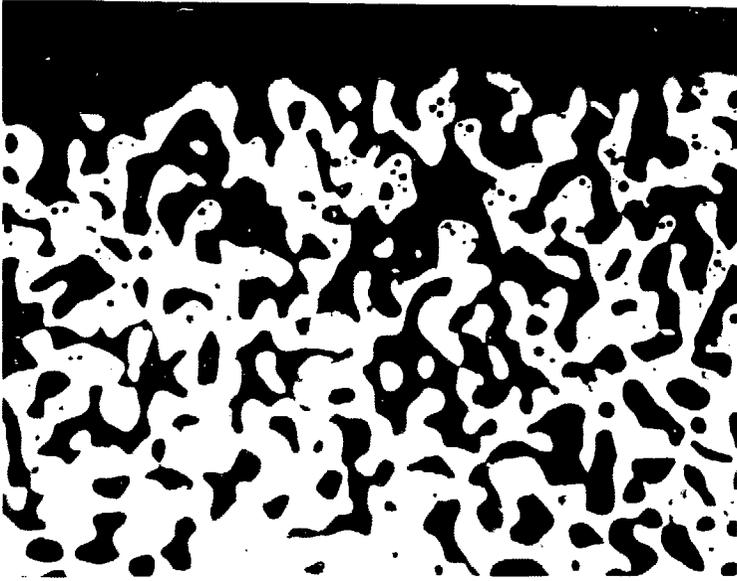
FIGURE 8   Surface of UO₂ sample oxidized in air at 1900°C showing
results of volatilization
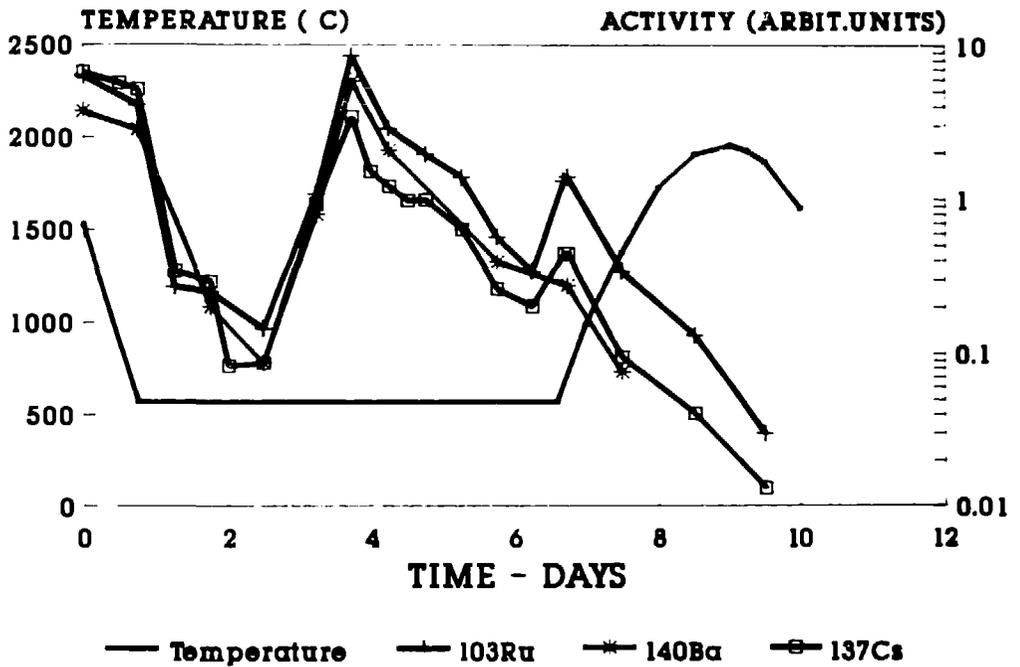
FIGURE 9   Temperature history and fission-product release from
the Chernobyl reactor.