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AUTHOR

D. R. Dickinson

T. F. Demmitt

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CRUD DEPOSITION IN KER LOOPS AT pH 10 LiOH

D. R. Dickinson and T. F. Demmitt

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CRUD DEPOSITION IN KER LOOPS AT pH 10 LiOH

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INTRODUCTION

One of the problems which may be encountered in the operation of NPR, or of any similar pressurized-water reactor, is the deposition of crud in the reactor core, particularly on the surfaces of the fuel elements. This crud consists primarily of iron oxides resulting from the corrosion of the piping. It has generally been found to deposit preferentially in a radiation field such as is present in the reactor core. Such deposition is undesirable for two reasons. First, the crud will become activated, and on subsequent release may create radioactivity levels in the ex-reactor components of the primary loop high enough to be a hazard to maintenance and operating personnel. Secondly, the crud deposit is a poor conductor of heat, and even a rather thin film can raise the cladding temperature by 100 - 200°C and result in accelerated corrosion of the cladding.

SUMMARY

Two instances of major crud deposition have recently been encountered in the in-reactor KER loops during operation at pH 10 LiOH.

The test in KER-1 (carbon steel) lasted 2 weeks and followed a cleaning of the loop with ammonium citrate. Crud concentration in the water was abnormally high; the last part of the test was at low temperature which resulted in even higher crud concentration. A fairly heavy dark-brown crud deposit was found both on Zircaloy-clad fuel elements and on the unautoclaved Zircaloy sleeves surrounding them.

The test in KER-2 (stainless steel) lasted 4 months and followed installation of new heat exchangers. Water quality during the test was good, except for one instance when cleaning solution was inadvertently introduced during the cleaning of KER-1. A deposit similar to that in KER-1 was found on the sleeves, but very little on the fuel elements.

These two instances are the first of any significant crud deposition in the KER loops during high pH operation.

Previous KER Experience

Prior to the two tests described below, crud deposition has not been encountered during high pH operation of the KER loops. Loop 1 (carbon steel) has operated at pH 10 LiOH since its initial start-up in February, 1958. Loops 2, 3, and 4 (stainless steel) have operated at pH 10 LiOH since November, 1958, October 1959, and February 1960 respectively. Outlet temperatures during these periods ranged from 200 to 288 C. During and between these tests, process water was on several occasions introduced into the in-reactor portion of the loops. During this time no significant amount of crud has been observed on discharged fuel elements or spacers, or caused any serious problem of radioactivity release as crud bursts. The characteristic shiny black autoclave film was commonly visible on the discharged elements. In a couple of instances, the

elements were coated with a thin dull soot-like film, thinner and considerably different in appearance than the iron-oxide deposit described in the following section.

The stainless steel loops had formerly operated at neutral and reduced pH. At pH 6, the fuel elements and spacers (Zircaloy, stainless steel and aluminum) were covered with a moderately heavy red-brown rust-like film. At pH 4.5 with phosphoric acid, heavy deposition of a similar film occurred on Zircaloy and aluminum fuel cladding and on stainless-steel and aluminum spacers.

Test K-1-16

This test immediately followed a period of non-standard loop conditions. The KER-1 loop had been modified by the installation of new larger heat exchangers and pumps and other minor changes. Following this modification several tests without fuel elements were conducted in the loop in the period November 12, 1962 to February 16, 1963. These tests involved intentional rusting of the loop piping, tests of procedures for cleaning the piping, and the use of ammonium hydroxide for pH control. On January 29 the ex-reactor portion of the loop was cleaned with ammonium citrate, which removed the rust and film from the piping surfaces, and established a fresh surface for subsequent operation. This cleaning was followed by 4 days clean-up with NH_4OH , 8 days at pH 10 LiOH at 180-200 C, during which time the crud concentration in the water were normal. After this the loop was down 5 days for maintenance.

The loop was charged on February 16, 1963, with twelve 17.3-inch NIE-1 fuel elements contained in Zircaloy sleeves. This test ran for 5 days at high temperature (outlet temperature of 250 C maximum, 230 C average), followed by 9 days at low temperature (90 C outlet) due to a leak in the front nozzle. The fuel was discharged on March 4. During the test the water was kept at pH 10 with LiOH , except for a short period during the first day of the test when some acidic cleaning solution trapped in the lines was valved in causing the pH to drop to 7.2. The crud concentration in the water was abnormally high during the test, particularly during the latter period at reduced temperature. Further details of the water quality before and during this test are given in HW-77356.⁽¹⁾

The day after discharge, the fuel elements were removed from their sleeves and examined through the telescope at the 10-foot level of the KE examination basin. All were covered with a dark-brown crud film of moderate intensity. The amount of crud was probably small, but was sufficient to cover the surface, except on a portion of the surface of one element where the black autoclave film could be seen. The sleeves, which had not been autoclaved, had about the same crud deposit as the fuel elements. The stainless steel spacers had a similar deposit, but a bit lighter and less uniform. There was little difference between stainless steel exposed in-flux and out-of-flux.

⁽¹⁾ Larrick, A.P., T.F. Demmitt, and V.F. FitzPatrick, Chemical Cleaning and Operation of the KER-1 Test Facility, 11/12/62 through 3/5/63, HW-77356, March 31, 1963. Unclassified.

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Photographs of the crud deposit on the upstream, center, and downstream fuel elements in the charge are shown in Figures 1, 2, and 3, respectively. The slight differences in appearance between these three elements are probably due primarily to slight differences in lighting since visual observation indicated little difference in crud deposit with position. The shiny metallic spots in these photographs are due to scraping the film in handling after discharge. Figure 4 shows a typical Zircaloy sleeve. The red-brown deposit seen on the carbon-steel supports resulted from contact with process water in the storage basin and was not present when discharged.

The operation at low temperature during the latter part of the test resulted in high concentration of radiolytic oxygen and hydrogen peroxide in the coolant, since at low temperature the recombination of the products of radiolysis is slow. It is believed that the adherent magnetite (Fe_3O_4) film on the piping was oxidized under these conditions to non-adherent ferric oxide (Fe_2O_3), and that this was the cause of the greater concentration of crud encountered during this period at low-temperature. It is therefore likely that the amount of material deposited on the elements would have been much smaller if this low-temperature operation had not been encountered. However, this should not be considered as the sole cause of the crud deposition, since on at least two previous occasions this loop has operated at low temperature at pH 10 LiOH at the end of a fuel exposure without any crud deposition. It seems likely that the magnetite film on the piping was never fully restored to its normal equilibrium condition following the last cleaning, and that the rate of release of corrosion products from the piping surfaces were therefore abnormally high during the test. The contamination with acidic cleaning solution undoubtedly also aggravated this condition.

Test K-2-15

Eight 17.3-inch Zircaloy-clad NIE-1 fuel elements in unautoclaved Zircaloy sleeves were charged in KER-2 (a stainless steel loop) on November 27, 1962, and discharged March 25, 1963. These fuel elements and sleeves were the same as those irradiated in Test K-1-16. Prior to the start of this test KER-2 had been down since March 29, 1962, for a modification similar to that conducted on KER-1. During the test, the water was maintained at pH 10 with LiOH. The water quality was good with the one exception noted below. The outlet temperature was 210-235 C for 54 days during the early part of the test, and 175-185 C for 31 days during the latter part of the test; the loop also had 34 days of low-temperature operation when the reactor was down and during shut-down and start-up.

On January 29, 1963, during reactor operation with the loop at high temperature, some ammonium citrate cleaning solution was inadvertently added to the re-circulating coolant with the feedwater stream during feed-and-bleed operation. Within a few hours the pH decreased from 10 to 6.5, the specific resistance decreased to 1.3×10^5 ohm-centimeters, the total solids concentration increased from about 8 ppm to about 225 ppm, and a serious crud burst occurred that increased the coolant activity level considerably. Magnetite particles were observed in the coolant confirming the crud burst. The loop water quality prior to this incident had been normal.

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Corrective action taken as soon as the chemical contamination was discovered included: (1) flushing and refilling the storage tank with deionized water to remove the cleaning solution, (2) adding lithium hydroxide to the recirculating coolant to raise the pH, and (3) increasing the feed-and-bleed purification rate to facilitate rapid dilution of the recirculating coolant stream. These actions were extremely effective as evidenced by the fact that the coolant had returned to near normal conditions within about 24 hours. At this time the pH was 10, the total solids concentration was 15 ppm, the specific resistance was 4×10^4 ohm-centimeters, the coolant activity was near normal, and there was no further evidence of magnetite particles in the coolant samples. The water quality conditions continued to improve during subsequent operation; thus there was no apparent permanent damage to the system as a result of this incident. A more detailed discussion of the loop water quality prior to, during, and after this incident is described in HW-77388.(2)

The charge was visually examined the day after discharge using the telescope at the 10-foot level of the KE examination facility. The unautoclaved Zircaloy-2 sleeves were covered with a fairly heavy uniform dark-brown crud deposit much like that found on the fuel elements and sleeves from K-1-16. No effect of turbulence on the intensity of deposition was noticed at the ends, near the supports, or where the OD was cut down. There was no indication of flaking off of the deposit. The fuel elements, by contrast, had either no crud, or only a very light thin crud film below which the shiny black autoclave film could still be seen.

The crud deposition in this test is harder to explain than that in K-1-16, since the test was generally characterized by good water quality. The modification of the loop prior to the test, particularly the installation of new heat exchangers, introduced fresh steel surfaces which would have corroded and released corrosion product at an abnormally high initial rate for a few days until a stable magnetite film could be formed. The introduction of cleaning solution probably also contributed to an abnormal formation of crud. The relative absence of crud on the fuel elements compared to the sleeves is puzzling. Previous experience, both at Hanford and elsewhere, indicates that crud is more apt to deposit on fuel than on non-fuel surfaces.

Since the charge operated for about two months with good water following the introduction of cleaning solution, it is possible that a heavier deposit originally formed and that some of it was slowly removed during subsequent operation.

Future Work

The occurrence of crud deposition in these two tests points up the need for continued study to determine what conditions which may be encountered in NPR might lead to crud problems and what can be done to reduce or eliminate crud deposition in these cases. Crud concentration in the coolant and its deposition

(2) FitzPatrick, V.F., Dibasic Ammonium Citrate Contamination of the KER-2 and KER-4 Loops. HW-77388, 5-3-63, Unclassified.

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on the fuel charge will therefore continue to be monitored in all KER tests. In order to assess the seriousness of crud deposition such as was observed during these tests, a thermocouple slug is needed to measure the resulting increase in cladding temperature.

Dean R. Dickinson

D. R. Dickinson
Coolant Systems Development Operation
Reactor and Fuels Laboratory
HANFORD LABORATORIES

Thomas F. Demmitt

T. F. Demmitt
Coolant Systems Development Operation
Reactor and Fuels Laboratory
HANFORD LABORATORIES

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FIGURE 1

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FIGURE 3

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FIGURE 4

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