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CORROSION PRODUCT STUDY
BY SCANNING ELECTRON MICROSCOPE

November 1969

AEC RESEARCH &
DEVELOPMENT REPORT

P. J. Lemmitt 31475-1704K		NOV 24 1969	5/17/71

BNWL-1184

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UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

3 3679 00061 5304

BNWL-1184
UC-80, Reactor
Technology

CORROSION PRODUCT STUDY
BY SCANNING ELECTRON MICROSCOPE

By

T. J. Kabele
Chemistry Research Department

and

3 L. Daniel
Metallurgy and Ceramics Department
Chemistry and Metallurgy Division

November 1969

Battelle Memorial Institute
Pacific Northwest Laboratories
Richland, Washington 99352

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

CORROSION PRODUCT STUDY BY
SCANNING ELECTRON MICROSCOPE

ABSTRACT

Changes in the form and composition of the corrosion products on the surfaces of four typical N-Reactor materials as functions of time and coolant flow rate were observed using a scanning electron microscope. Zircaloy-2, Inconel, 304-stainless steel and mild steel coupons were exposed to deionized, deoxygenated, pH-10 ammonia water at 280°C and 1000 psi. Exposures were one hour to nine weeks at flow rates from zero to 30 ft/sec.

A great variety of corrosion products (both in form and composition) were observed. A detailed description of these corrosion products is presented along with micrographs and X-ray spectrograph data,

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CORROSION PRODUCT STUDY BY SCANNING ELECTRON MICROSCOPY^(a)

T. J. Kabele and J. L. Daniel

INTRODUCTION

Underlying every discussion of corrosion of reactor materials and the deposition of corrosion products on reactor surfaces is the question of the microstructure of the corrosion products and the relation of this structure to the system environment. A knowledge of the dependence of the microstructure of corrosion products upon environmental variables can lead to an understanding of the mechanisms responsible for the formation of corrosion products and crud deposits. The recent developments in scanning electron microscopy have resulted in a powerful new tool, ideally suited to the study of the structure of corrosion product deposits. This research program was undertaken to evaluate this technique as a means of defining some of the system variables which directly relate corrosion product formation, crud deposition, and microstructure in the Hanford N Reactor.

The specific goals of this study were to observe the form and composition of the corrosion products on the surfaces of four materials as functions of exposure time and coolant flow rate, and to determine, if possible, which corrosion products were deposited on the coupons and which were grown in situ. From this information about the differences and/or similarities between these two basic forms of corrosion products a mechanism for the overall accumulation of corrosion products on a metal surface might be indicated.

The experimental program consisted of exposing small coupons of representative reactor materials at typical N Reactor conditions for various lengths of time and flow rates. The coupons were then examined with the scanning electron microscope. On some coupons an X-ray spectrometer was used to identify the elemental constituents of the corrosion products present. The structural changes of the corrosion products and the deposits were thus observed as functions of time, material, and flow environment.

(a) This research program was sponsored by Douglas United Nuclear, Inc., Richland, Washington.

This report presents, in detail, the observations made during this research program and suggests possible interpretations of those observations. The primary worth of this work lies in the careful study of the surface microstructure of the test coupons, since from a knowledge of the microstructure and local compositions one can begin to elucidate the mechanisms responsible for the formation of a layer of corrosion products on a metallic surface. New questions have been raised by this work and the complex nature of corrosion product formation and crud deposition is emphasized.

EXPERIMENTAL

COUPON EXPOSURE

The four materials studied in this work were mild steel (ASTM A-415), 304-stainless steel, Inconel, and Zircaloy-2 (ASTM B-352-60T). Coupons of these materials, 0.5 inch square and 60 mils thick, were exposed to deionized, deoxygenated, pH-10 ammonia water at 280°C and 1000 psi. Exposure times were one hour, one day, eight days, five weeks, and nine weeks. Two groups of the coupons were exposed in a stainless steel, recirculating water loop at bulk stream fluid velocities of 10 ft/sec and 30 ft/sec. Other coupons were exposed in a stainless steel autoclave with a refreshment rate of one-fifth of a gallon per hour, which is nearly a non-flow condition. Water chemistry, temperature, pressure, and exposure times were the same for the loop and the autoclave. A photograph and a schematic drawing of the recirculating water loop are presented in Figure 1.

The mild steel, stainless steel, and Inconel coupons were prepared by mechanically abrading their surfaces with 4/0 3M Polishing Paper, then cleaning with alcohol. The Zircaloy coupons were acid etched, cleaned, and autoclaved in steam for four days at 400°C and 1500 psi, a pre-film treatment commonly used for zirconium alloys before in-reactor use.

The coupons, held in the test loop in stainless steel holders, were oriented so that the water flowed parallel to the flat surface of the coupons. The Inconel and Zircaloy coupons were in parallel positions in one holder upstream of the second holder containing the steel coupons. With a coolant flow rate of 10 ft/sec, coupons were withdrawn after exposures of one hour, one day, eight days, five weeks and nine weeks. At a coolant flow rate of 30 ft/sec, coupons were withdrawn after one week and two weeks.

The coupons undergoing autoclave tests were placed in a stainless steel holder and subjected to the same conditions as those in the loop, except for the zero flow rate.

The experiment was designed so that flow rate, exposure time, and material were the independent variables while changes in the coupon surface topography and microstructure were the dependent variables. Upon removal from the autoclave or the loop the coupons were air dried at room temperature. Scanning electron microscope examination of the coupons followed.

MICROSCOPIC EXAMINATION

A Model JSM-2 Scanning Electron Microscope from the Japan Electron Optics Laboratory Company, U.S.A., was used in the microscopic examinations of the sample coupons. This instrument allowed the examination and analysis of the physical details of as-formed sub-micron components of materials for the first time. In principal, the scanning electron microscope operates in a manner similar to the more familiar electron microprobe analyzer. However, the electron beam is about 100 Å in diameter at the point of contact with the specimen, thus allowing a high resolution of specimen surface detail. The primary beam generates several types of useful information; the most commonly used is the emission of secondary electrons, which are collected on a scintillation detector and caused to modulate the CRT of a display system. As the primary electron beam scans the sample in synchronism with the CRT, an image of the surface of the specimen is drawn with a resolution of about 250 Å. At the same time, X-ray energy characteristic of the elements comprising the sample surface is emitted and collected by a solid-state detector. These signals can be analyzed with an energy analyzer and the composition of the surface thus determined. The combination of these two types of information simultaneously has for the first time allowed analysis of the sub-micron components as they are being viewed in microscopy.

One of the major inherent advantages of scanning electron microscopy is the very large depth of focus. This feature makes it possible to examine most materials with no further preparation beyond their actual production. Non-conducting materials require a vacuum-deposited gold coating to prevent

electrical charge buildup, but this gold coating was unnecessary for the present experiments. The size of the coupons used in this program (0.5 inch square x .060 inch) was such that they could be transferred from the loop or the autoclave to the microscope with no further preparation. The views shown on the micrographs are the coupons' surfaces exactly as they developed during their exposure.

RESULTS

In this section, representative photomicrographs of each of the coupons studied are presented. Most of the micrographs were taken at a magnification of 100X, 1000X, 3000X, or 10,000X, to enable comparisons, at the same magnifications, of the features of the numerous coupons. Other magnifications (usually higher) were used to present particularly fine microstructure.

The X-ray data are presented on bar graphs. These data are semi-quantitative; the bar graphs represent relative X-ray peak heights for the various elements displayed. Since no elemental calibrations were attempted, peak heights may vary with each determination and only relative comparisons of compositions can be made. Elements with atomic number thirteen (aluminum) or higher can be detected. Therefore, when the "composition" of a particular corrosion product is given in this report, its probable presence as an oxide is assumed.

In presenting the results of the microscopic examination of the coupons, certain terms must be defined. "Corrosion products" refers to all species observed on the metal surfaces without regard to the origin of these products. "Corrosion product deposit" or "deposits" refer to corrosion products transported to the surface in question from some other source and are synonymous with "crud". "Local corrosion products" refers to in situ corrosion product growth. "Crystalline" is used to denote a material which exhibits external evidence of a regular or a faceted structure, where "amorphous" connotes a formless mass, which exhibits no external evidence of crystallinity; such a mass might possess a regular crystalline internal structure, but the crystalline nature is not evident from surface examination at magnifications to 30,000X.

FILTER

Since the corrosion products were of primary concern in this study, the specimens will be discussed in order of increasing amount of observed corrosion products. The first area examined was a silver filter paper which was placed in the effluent (bleed) line of the recirculating water loop. Although highly convenient to use, this was not an ideal filter location since the flow rate was very slow (about two gallons per hour) and, therefore, the heavier, larger particles probably were not swept into the filter at a representative rate and only a small fraction of the total coolant entrained in the system passed the filter position. Nevertheless, the filter collected a large volume of solids.

Figure 2 shows results of the exposure of 1.2-micron silver filter paper. Micrograph 1952 shows the silver filter paper in an unexposed clean condition, while the other three micrographs show the results of a two-hour exposure. Several forms of deposit are observable, including both amorphous and crystalline material and some needle-like elongated crystals.

Figure 3 shows a stereo view of the 0.5-micron silver filter after a two-hour exposure. The average composition of the deposit, represented by the data for the area within the white circle, is rich in iron and silver, the material from which the filter was made. The crystalline material is very rich in iron, with about a three-to-one distribution between iron and chromium. The flat plate-like material with the pebbled surface contains about equal proportions of iron and chromium.

ZIRCALOY-2

The most "unreactive" substrate material studied in this work was the Zircaloy-2. The pre-filmed condition of the Zircaloy-2 coupons is shown in Figure 4. The lacy network of corrosion products which appears in the grain boundaries is shown in detail in micrograph 331. Note that there are two types of corrosion products, needle-like material and spherical-shaped "pebbles". The darker background material is composed of zirconium. Both "needles" and "pebbles" show about a 3 to 1 ratio between zirconium and chromium, and they both contain copper. However, the pebbles appear to contain much more copper than do the needles and, in addition, the pebbles are higher in copper than in zirconium. The presence of copper

cannot be explained from the composition of the coupons themselves, but between 1 and 10 parts per million of copper was found in the feed water used for all these experiments. This apparently accounts for the presence of copper in the corrosion products shown on the Zircaloy-2 coupons.

However, the needles and pebbles on the Zircaloy-2 coupons did not remain fixed in place during the flowing test. As shown in Figure 5, after just one day of flow at 10 ft/sec the needles and pebbles had largely disappeared from the surface of the coupon. Only the amorphous form of material remains on the Zircaloy coupon, shown in Figure 6. After nine weeks of flow at 10 ft/sec even less material remains on the surface of the Zircaloy-2 coupon, the remaining material being amorphous in character. If the flow rate is increased to 30 ft/sec, after only two weeks of exposure no material is visible on the surface of the Zircaloy-2 coupon. X-ray analysis of this surface shows only zirconium. It is postulated that the apparent light and dark areas relate to different oxidation conditions of the surface rather than differences in composition. The gradual disappearance of the copper-bearing corrosion products from the Zircaloy-2 coupons was not observed on the other materials tested.

Coupons of Zircaloy-2 were also exposed for varying lengths of time in a stainless steel autoclave under the same conditions of temperature, pressure, and water chemistry as those specimens exposed in the recirculating water loop. Figure 7, the results of a one-day autoclave exposure, shows a network of corrosion products similar to that seen on the coupons exposed in the recirculating system. After nine weeks in the autoclave the deposit on the Zircaloy-2 coupons is decidedly crystalline in nature, largely in the form of cubes. X-ray data presented in Figure 8 show that the cubes contain a significant concentration of chlorine. Chlorine was detected in no other corrosion deposit in this work; the source of the chlorine here is unknown.

INCONEL

The pre-test condition and the composition of the Inconel coupons used in these tests are shown in Figure 9. Micrograph number 304 shows that there is little or no material in any of the cracks or crevices of the polishing marks on the coupon. An exposure of one day in the recircu-

lating loop at 10 ft/sec (Figure 10) produces only a light corrosion product coating, most of which consists of roughly spherical particles.

After an exposure period of nine weeks a heavier layer of corrosion products has developed, as shown in Figure 11. This layer actually comprises two different zones; a surface zone composed of closely packed, uniform crystals, and a zone of crystalline material scattered above the surface in a random manner. The surface crystals contain about twice as much iron as was originally present in the Inconel (Figure 12), while the base material is severely depleted in nickel; some small needle-like structures on the surface are intermediate in composition between the base material and the deposits. No copper was found on any area of this coupon. When the flow rate was increased to 30 ft/sec (Figure 13) the surface was effectively washed clean and almost no deposition occurred.

After a one-day exposure in the autoclave only a very light corrosion product layer was observed on the Inconel (Figure 14). After a nine-week autoclave exposure a heavy layer of large, well-formed crystals results (Figure 15), uniformly distributed over the base material. The composition and appearance of these crystals, many of which are octahedral in shape, are shown in Figure 16. While the base material has retained the composition of the original Inconel, the crystals contain about four times as much iron as the Inconel. This high iron concentration, together with the random position of these crystals in the upper layer of corrosion products, suggests that these crystals were deposited over a layer of corrosion products formed from the Inconel itself. The most probable source of these iron-rich crystals in this system was the stainless steel autoclave. Iron (and maybe some chromium and nickel) from the autoclave probably crystallized out in the boundary-layer above the Inconel yielding iron-rich crystals along with significant amounts of nickel and chromium.

STAINLESS STEEL

The 304-stainless steel coupons generally incurred somewhat more deposition than was evident on the Inconel or Zircaloy. As was true with the Inconel, no material was found in the cracks or crevices of the stainless steel coupon in the pre-test condition (Figure 17). After only a one-hour exposure in the recirculating water loop at 10 ft/sec

corrosion product deposits composed of amorphous, pebble-like, and needle-shaped materials were lightly and randomly distributed over the surface of the coupon (Figure 18). The needles and pebbles were similar to the corrosion products which occurred originally on the Zircaloy-2 specimens in the pre-filmed condition. After one day's exposure the deposit becomes more uniformly distributed over the coupon, although the character of the corrosion product deposit does not change (Figure 19). The needle-like structures are of the same metallic composition as the 304-stainless steel base (Figure 20). The pebble-like material, however, contains a high percentage of copper, with almost equal amounts of iron and chromium, and was probably crystallized from or formed in the flowing stream. The source of these deposits was probably the internal stainless steel walls of the loop. The needles may have formed in the boundary layer above the stainless coupon, or may be a deposit from the stainless steel of the loop, like the pebbles.

After a nine-week exposure in the recirculating water loop at 10 ft/sec the corrosion product deposit on stainless steel contains the same structures as after one day of exposure but a much heavier deposit has resulted (Figure 21). From the X-ray data (Figure 22), the pebble-like material now appears to be of the same composition as the original 304-stainless steel, but the base metal and the needles have increased their chromium content. Copper is no longer present in the pebbles. The increased chromium content of the corrosion products indicates that chromium was being transported in this system, but the source of this chromium is unknown.

After a two-week exposure of a stainless steel coupon in the recirculating water loop at 30 ft/sec (Figure 23) the deposit appears to be much less concentrated than in the lower flow rate loop, as if it is being washed away as quickly as it was formed similar to the appearance of the Inconel and the Zircaloy.

The exposure of the 304-stainless steel coupons in the autoclave resulted in the most interesting crystalline corrosion product forms seen on any of the test coupons. After a one-day exposure of 304-stainless steel in an autoclave (Figure 24) a light uniform layer of well formed, octahedral crystals, one to three microns in size, is

distributed over a base material composed of very tightly packed octahedral crystals, about one-tenth to one-half micron in size. Figure 25 shows some of the octahedral crystals and the base material at a magnification of 40,000X; the metallic composition of the base material is nearly the same as the original 304-stainless steel, but the large octahedral crystals are much lower in chrome and nickel; a trace of copper is also present. In some regions the large octahedral crystals have a freckled appearance, particularly evident in stereo micrographs (Figure 26) and at high magnification (Figure 27). These freckled octahedral crystals are generally of composition similar to the smooth crystals seen in Figure 25, except for a somewhat higher chromium content, suggesting that the freckled structure is a chromium-rich deposit. The base material still has approximately the same composition as 304-stainless steel.

Since the preferred habit of magnetite is an octahedral shape, these crystals are probably magnetite with some substitution of nickel, chromium, and copper for iron in the crystal lattice.

The results of a nine-week autoclave exposure of a 304-stainless steel coupon are shown in Figure 28. The corrosion products seen on this coupon are primarily of two types, amorphous and a cubic crystalline structure. As shown in Figure 29, the base structure has the same metallic composition as the original stainless steel, although its form is crystalline and similar to that seen on the one-day autoclave exposure. The amorphous material shown in micrograph No. 1650 is of similar composition.

The cubic crystals shown in these micrographs, however, contain primarily copper, with lesser amounts of iron, chrome, and nickel in the approximate proportions expected in stainless steel. These cubes occur in several degrees of perfection, all the way from a perfect cube to a nearly completely destroyed cube (Figures 29 through 32). It is interesting to note that the deterioration of the cubes begins in the center of the cube faces, proceeds to the center of the cube edges and then extends finally to the destruction of the entire cube.

MILD STEEL

The fourth material tested was a mild steel. The pre-test condition of the mild steel coupons (Figure 33) is similar to that for the stainless and the Inconel. After only one hour of exposure in the recirculating water loop at 10 ft/sec, the carbon steel coupon exhibits a prominent corrosion product (Figure 34) composed of amorphous material, needle-like structures and pebble-type structures.

After one day of exposure at 10 ft/sec the layer of corrosion products has grown heavier and more uniformly distributed (Figure 35) although the primary forms of the corrosion product deposit remain unchanged; the general appearance is the same as that seen for similar exposure conditions on stainless steel. All forms of the corrosion product deposit are composed of iron and copper with the ratio between the two elements varying (Figure 36); the pebbles are copper-rich while the needles are iron-rich and the base material is almost entirely iron (undoubtedly in oxide or hydroxide form) with a slight trace of copper.

The deposit grows heavier with continued exposure up to eight days, five weeks (Figure 37), and nine weeks (Figure 38).

Pebble-like structures become the primary form of the corrosion product deposit, although some needle-like material also remains. After nine weeks of exposure the composition of the components is essentially unchanged (Figure 39).

The influence of a higher flow rate is shown in Figure 40, which shows a carbon steel coupon after a two-week exposure at 30 ft/sec. The corrosion product deposit is of two forms, fuzzy balls distributed evenly over the coupon surface overlying a densely packed substrate which appears to be crystalline in form. The small fuzzy balls are composed of iron and copper with approximately twice as much copper present as iron. The substrate is composed entirely of iron.

The X-ray data give the important clues as to the origin of the deposits on the mild steel. Copper, nickel, and chromium are all present in the corrosion products distributed over the base material, which is primarily composed of iron. This indicates that these

corrosion products are from an external source, probably the loop surfaces and the feed water copper impurity. The base material appears to be an iron oxide formed from the corrosion of the mild steel coupon and hence no significant quantities of copper, chromium, or nickel should be found in it.

The coupons of mild steel exposed in the autoclave exhibited an entirely different form of corrosion products. A one-day exposure in the autoclave produces corrosion products consisting of a layer of loosely packed flocculent matter and pebbles overlying a base of closely packed material (Figure 41). As shown in Figure 42, the closely packed base material is composed of iron; the flocculent material is iron with a little copper and a trace of chromium; and the pebble-like material is composed of iron, chrome, and copper, with twice as much iron as the other two elements. The platelet shown in the center of micrograph 878 is composed primarily of iron with small amounts of chromium, nickel, and copper present. In areas of the same coupon (Figure 43) the corrosion products occur in two layers atop the densely packed crystalline substrate. The pair of stereo micrographs at the bottom of Figure 43 suggest that the upper two layers are somehow connected together although in this series of micrographs these layers appear to be broken up.

After further exposure (eight days and five weeks, respectively) in an autoclave, the deposit assumes an amorphous form and appears to grow heavier with time (Figures 44 and 45).

After a nine-week exposure a crusty broken layer of flocculent material overlies a base material composed primarily of closely packed octahedral crystals (Figure 46). The crusty, flocculent layer (Figure 47) is composed of small pebble-like structures cemented together to form the flocculent mass. The great amount of material found on the mild steel coupon suggests significant in situ production of corrosion products from the mild steel itself.

To complete the examinations, a stainless steel specimen holder clamp which had been in the recirculating water loop for approximately 10 years was examined (Figure 48). The light amorphous material is composed primarily of iron, with some chromium and nickel present. The

dark areas, presumed to be a substrate or base material, are composed primarily of iron and chromium with a small amount of nickel present.

DISCUSSION

The corrosion products present on the coupons occurred in a great variety of forms and compositions. However, several significant similarities and regular relationships were observed among the various forms.

The most striking observation was that most of the corrosion product species were within one order of magnitude in size, namely from about 0.2 micron to 2 microns. Material in the closely packed layers adjacent to the metallic surfaces of all but the Zircaloy coupon generally was smaller in size than the crystalline or flocculent material scattered in the upper layers of corrosion products. The latter appeared to be much less adherent to the substrate than the former, suggesting that the larger crystals are the result of a transport/deposition process while the thinner, more closely packed layer may represent in situ growth. In general, the larger crystallites or "clumps" were above the closely packed layer and were much less uniformly distributed over the sample than the finer material on the base metal. The pebble-like structure of much of the top deposit in the flow test specimens also suggests a transport/deposit mechanism with the smoothed edges resulting from tumbling and erosion during the transport.

The chemistry of the materials on the coupons was also interesting. Copper, originating as a trace impurity in the feed water, was found in various forms of the crystalline deposits on several of the coupons, particularly on the stainless and carbon steel. On the carbon steel, copper collected early in the flow tests (after one day) and remained on all the coupons thereafter, both in the autoclave and in the loop. The copper-bearing deposit originally on the Zircaloy-2 probably came from the stainless steel autoclave in which the Zircaloy was pre-filmed, but it completely disappeared from the Zircaloy coupons during flowing coolant tests. Apparently the copper is very mobile with an affinity for the steels; almost no copper was found on any of the silver filters or Inconel samples.

Even the elemental constituents of the coupons themselves proved to be quite mobile. For example, nickel appeared to be relatively

mobile, resulting in nickel depletion of the base metal of all Inconel coupons. The site for redeposition was not apparent; little or no nickel was detected on the Zircaloy-2 or carbon steel coupons. However, chromium was found in almost all of the deposits on carbon steel and Zircaloy-2. Obviously, some of the components of the crystalline and flocculent materials originated at some other site since neither carbon steel nor Zircaloy contain chromium initially. Likewise, the presence of copper in the deposits required more than the simple in situ oxidation of base metal.

All of these observations are interpreted to show that mass transport to and from each coupon and the water is taking place. In addition to the transport, there must be solution/dissolution phenomena occurring as well as redox chemical reactions. The mobility and materials preference shown by both trace elements and metal constituents clearly demonstrates the complexity of the corrosion chemistry in any reactor system in which many elements are present in trace quantities. Demonstrated also is the importance of complete analyses of all components before interpreting experimental data and the considerable difficulty of conducting a completely "clean" experiment.

The effect of flow rate on the corrosion products was clearly evident and took two forms. With decreasing flow rate (quiescent as opposed to flowing water), an increased quantity of crystalline corrosion products was observed. In the flowing system, pebble- and needle-like corrosion products were most common; in the autoclave, well-formed crystals predominated. Moreover, the crystals in the flowing system generally were somewhat smaller than in the autoclave, probably because of the thinner mass boundary layer on the loop coupons which contains less material with which to build larger crystals at any given nucleation site.

Increasing the flow rate of water over the coupons resulted in smaller amounts of randomly scattered clumps of corrosion products on the coupons, as though a "sweeping" action by the fluid was occurring. Specimens exposed at a flow rate of 30 ft/sec retained almost no deposits except a layer of rather fine, uniformly distributed corrosion products over the base metal.

CONCLUSIONS

The major conclusions to be drawn from this work are as follows:

1. The material of which a coupon is made strongly influences the amount of corrosion products found on the surface. In this study, increasing amounts of corrosion products were found on Zircaloy, Inconel, stainless steel and mild steel, in that order.
2. The flow rate of the fluid in contact with a coupon surface influences the physical form of the corrosion products, lower flow rates favoring a crystalline form.
3. Some of the metallic elements present in the metals (and fluid) are very mobile, transporting freely throughout the system. In this case, chromium, nickel, and copper appeared in most of the corrosion products, even though chromium and nickel were not present in the original base metal of two of the coupon materials and copper was originally present only in the feed water at 1 to 10 parts per million.
4. Corrosion products grown in situ and those deposited from other sources can both contribute significantly to the total corrosion product inventory on a metallic surface.

To elaborate, the "materials effect" was shown in this study by the lack of deposition on the Zircaloy coupons compared with that which occurred on the other materials, particularly the steels. Even after long exposures, very little corrosion product is deposited on the surface of the Zircaloy coupons; after only one hour, significant deposits are found on the steel. It would be interesting to examine the effect of pre-filming the Inconel and steel coupons before exposure in a manner similar to Zircaloy pre-treatment.

The flow rate probably exerts its influence through changes in the boundary layer thickness, fluid mixing, local concentration gradients above a coupon surface, etc., which affect mass transport and solution/dissolution phenomena. In addition, at high flow rates erosion may be important in limiting the growth and deposit of corrosion products on a surface.

The great mobility of the metallic elements seen in this study emphasizes the importance of mass transport phenomena in the buildup and maintenance of a corrosion product deposit. Moreover, the transport is probably very species dependent, as evidenced by the lack of steel corrosion products on the Zircaloy. When coupled with the solution phenomena, the mass transport is seen to be an extremely important and complex part of the total problem. This work also confirmed that both in situ corrosion and deposited corrosion products are significant contributors to the total corrosion product observed and each type was tentatively identified on specific sites. However, a much "cleaner" system with fewer unknown sources of crud would be necessary to study this problem.

FUTURE WORK

There are two general areas where further research could yield immediate dividends. First, experiments similar to those reported here but conducted in a more controlled system, e.g., a loop lined with a single material or an inert material, could provide some quantitative information on the exchange of material between the fluid and a metal surface, especially if coupled with coupon weight-gain data. The materials effect should be investigated specifically to determine which elements preferentially deposit on other metals or surface types. The behavior of trace elements such as nickel, dissolved in the aqueous phase, should also be examined.

The other profitable area is the utilization of existing nuclear reactors as sources of corrosion product specimens. Materials from an operating nuclear reactor should be studied to determine the type and composition of corrosion product deposits present. The presence of ionizing radiation in the reactor environment is likely to exert a very significant influence on the corrosion product behavior.

BNWL-1184

APPENDIX

A-1

BNWL-1184

A. 350°C Isothermal Loop

B. Loop Schematic

FIGURE 1

A-2

BNWL-1184

1.2 Micron Silver Filter Paper

(Clean)

Neg. No. 1952

1000X

(2 hr Exposure)

Neg. No. 1784

1000X

Neg. No. 1785

3000X

Neg. No. 1786

10,000X

FIGURE 2

0.5 Micron Silver Filter, 2 Hr Exposure

FIGURE 3

A-4

BNWL-1184

Zircaloy-2, Pre-Test Condition

Neg. No. 264

100X

Neg. No. 265

1000X

Zr

Neg. No. 331

10,000X

FIGURE 4

Zircaloy-2, 1 Day at 10 ft/sec

FIGURE 5

A-6

BNWL-1184

A. Zircaloy-2, 9 Weeks at 10 ft/sec

Neg. No. 1476

1000X

Neg. No. 1477

3000X

B. Zircaloy-2, 2 Weeks at 30 ft/sec

Neg. No. 1718

100X

Neg. No. 1719

1000X

FIGURE 6

Zircaloy-2, 1 Day in Autoclave

Neg. No. 1219

100X

Neg. No. 1220

1000X

Neg. No. 1221

10,000X

FIGURE 7

Zircaloy-2, 9 Weeks in Autoclave

Neg. No. 1492

1000X

Neg. No. 1493

3000X

Neg. No. 1489

10,000X

FIGURE 8

A-9

BNWL-1184

Inconel , Pre-Test Condition

Neg. No. 303

100X Neg. No. 304

1000X

Neg. No. 305

3000X
FIGURE 9

A-10

BNWL-1184

Inconel, 1 Day at 10 ft/sec

Neg. No. 1465

100X

Neg. No. 1466

1000X

Neg. No. 1467

3000X

Neg. No. 1468

10,000X

FIGURE 10

A-11

BNWL-1184

Inconel, 9 Weeks at 10 ft/sec

Neg. No. 1516

1000X

Neg. No. 1517

3000X

Neg. Nos. 1518-1519 (Stereo Pair)
FIGURE 11

10,000X

A-12

BNWL - 1184

Inconel, 9 Weeks at 10 ft/sec

Neg. Nos. 1910-1911 (Stereo Pair)
FIGURE 12

3000X

Inconel, 2 Weeks at 30 ft/sec

A-13

BNWL-1184

1000X

Neg. No. 1721

100X

Neg. No. 1720

FIGURE 13

Inconel, 1 Day in Autoclave

Neg. No. 1473

100X

Neg. No. 1474

1000X

FIGURE 14

A-15

BNWL-1184

Inconel, 9 Weeks in Autoclave

Neg. No. 1500

1000X

Neg. No. 1501

3000X

Neg. Nos. 1502-1503 (Stereo Pair)

10,000X

FIGURE 15

Inconel, 9 Weeks in Autoclave

Neg. No. 1504

3000X

Neg. No. 1505

15,000X

FIGURE 16

A-17

BNWL-1184

304-Stainless Steel, Pre-Test Condition

Neg. No. 299

100X

Neg. No. 300

1000X Neg. No. 301
FIGURE 17

3000X

A-18

BNWL-1184

304-Stainless Steel, 1 Hr at 10 ft/sec

Neg. No, 43.2

100X

Neg. No. 433

1000X

Neg. No. 434

3000X

FIGURE 18

304-Stainless Steel, 1 Day at 10 ft/sec

Neg. No. 881

100X

Neg. No. 882

1000X

Neg. No. 883

3000X

Neg. No. 884

10,000X

304-Stainless Steel, 1 Day at 10 ft/sec

FIGURE 20

A-21

BNWL-1184

304-Stainless Steel, 9 Weeks at 10 ft/sec

Neg. No. 1520

100X

Neg. No. 1521

1000X

Neg. No. 1522

3000X

Neg. No. 1523

10,000X

FIGURE 21

304-Stainless Steel, 9 Weeks at 10 ft/sec

FIGURE 22

A-23

BNWL-1184

304-Stainless Steel, 2 Weeks at 30 ft/sec

Neg. No. 1722

100X

No. 1723

1000X

Neg. No. 1724

3000X

Neg. No. 1725

10,000X

FIGURE 23

304-Stainless Steel, 1 Day in Autoclave

Neg. No. 988

1000X Neg. No. 1957

3000X

Neg. Nos. 1065-1066 (Stereo Pair)
FIGURE 24

20,000X

304-Stainless Steel, Magnetite Crystals

Neg. No. 1027

FIGURE 25

40,000X

304-Stainless Steel, 1 Day in Autoclave

Neg. No. 1193

100X

Neg. No. 1194

1000X

Neg. Nos. 1195-1196 (Stereo Pair)

10,000X

A-27

BNWL-1184

304-Stainless Steel, Magnetite Crystals

Neg. No. 1212

FIGURE 27

40, 000X

304-Stainless Steel, 9 Weeks in Autoclave

Neg. No. 1573

100X

Neg. No. 1568

1000X

Neg. No. 1569

3000X

Neg. No. 1650

10,000X

304-Stainless Steel, 9 Weeks in Autoclave

FIGURE 29

A-30

BNWL-1184

304-Stainless Steel, 9 Weeks in Autoclave

Neg. Nos. 1881-1882 (Stereo Pair)

20,000X

Neg. Nos. 1879-1880 (Stereo Pair)

20,000X

FIGURE 30

A-31

BNWL-1184

304-Stainless Steel, 9 Weeks in Autoclave

Neg. No. 1875

20,000X

Neg. No. 1575

20,000X

Neg. Nos. 1572-1576 (Stereo Pair)
FIGURE 31

10,000X

304-Stainless steel, 9 Weeks in Autoclave

A-32

BNWL-1184

20,000X

Neg. Nos. 1883-1884 (Stereo Pair)

FIGURE 32

A-33

BNWL-1184

Carbon Steel, Pre-Test Condition

Neg. No. 261

100X

Neg. No. 262

1000X

Fe

Neg. No. 263

3000X

FIGURE 33

A-34

BNWL-1184

Carbon Steel, 1 Hr at 10 ft/sec

Neg. No. 597

1000X

Neg. No. 599

3000X

Neg. No. 598

10,000X

FIGURE 34

A-35

BNWL-1184

Carbon Steel, 1 Day at 10 ft/sec

Neg. No. 696

1000X

Neg. No. 695

3000X

Neg. Nos. 693-694 (Stereo Pair)

10,000X

FIGURE 35

Carbon Steel, 1 Day at 10 ft/sec

FIGURE 36

A. Carbon Steel, 8 Days at 10 ft/sec

Neg. No. 1698

3000X

Neg. No. 1699

10,000X

B. Carbon Steel, 5 Weeks at 10 ft/sec

Neg. No. 1694

3000X

Neg. No. 1695

10,000X

FIGURE 37

Carbon Steel, 9 Weeks at 10 ft/sec

Neg. No. 1688

100X

Neg. No. 1689

1000X

Neg. No. 1690

3000X

Neg. No. 1691

10,000X

Carbon Steel, 9 Weeks at 10 ft/sec

FIGURE 39

A-40

BNWL-1184

Carbon Steel, 2 Weeks at 30 ft/sec

Neg. No. 1735

1000X

Neg. No. 1736

3000X

Neg. No. 1737

10,000X

FIGURE 40

A-41

BNWL-1184

Carbon Steel, 1 Day in Autoclave

Neg. No. 873

100X

Neg. No. 874

1000X

Neg. Nos. 875-876 (Stereo Pair)

3000X

FIGURE 41

Carbon Steel, 1 Day in Autoclave

Neg. No. 876

3000X

Neg. No. 878

10,000X
FIGURE 42

A-43

BNWL-1184

Carbon Steel, 1 Day in Autoclave

Neg. No. 747

100X

Neg. No. 754

5000X

Neg. Nos. 748-749 (Stereo Pair)

1000X

FIGURE 43

A-44

BNWL-1184

Carbon Steel, 8 Days in Autoclave

Neg. No. 1709

100X

Neg. No. 1710

1000X

Neg. No. 1711

3000X

Neg. No. 1712

10,000X

FIGURE 44

A-45

ENWL-1184

Carbon Steel, 5 Weeks in Autoclave

Neg. No. 1713

100X

Neg. No. 1714

1000X

Neg. No. 1715

3000X

Neg. No. 1717

10,000X

FIGURE 45

Carbon Steel, 9 Weeks in Autoclave

Neg. No. 1651

100X

Neg. No. 1652

1000X

Neg. No. 1653

3000X

Neg. No. 1656

10,000X

FIGURE 46

A-47

BNWL-1184

Carbon Steel, 9 Weeks in Autoclave

Neg. No. 1684

1000X

Neg. No. 1685

3000X

Neg. Nos. 1686-1687 (Stereo Pair)

10,000X

FIGURE 47

Specimen Clamp, Stainless Steel

BNWL-1184

Neg. No. 1751

100X

Neg. No. 1752

1000X

Neg. No. 1753

3000X

FIGURE 48

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