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**AQUEOUS CORROSION OF URANIUM FUEL-ELEMENT
CORES CONTAINING 0 TO 20 w/o ZIRCONIUM**

by

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AQUEOUS CORROSION OF URANIUM FUEL-ELEMENT
CORES CONTAINING 0 TO 20 w/o ZIRCONIUM

Daniel R. Grieser and Eugene M. Simons

A description is given of the design and operation of a windowed autoclave system employed in the study of corrosion by pressurized hot water. The device has been used to obtain time-lapse motion pictures of the swelling and rupture of deliberately defected zirconium-clad uranium specimens. A method is described by which corrosion rates were calculated from pressure and temperature measurements. A typical set of pictures taken during a test is presented, and corrosion rates are reported for uranium-0, 5, 10, 15, and 20 w/o zirconium alloys subjected to 600 F water.

INTRODUCTION

Increased interest in the use of water as a primary heat-transfer medium in solid-fuel reactors has prompted many studies of aqueous corrosion of reactor materials. Because unalloyed uranium is particularly susceptible to corrosion by water, considerable work has been done in an effort to circumvent the problem of fuel-element corrosion by alloying and cladding the uranium with resistant materials.

Zirconium has appeared as one of the promising alloying and cladding elements, for it has favorable nuclear properties and is exceptionally resistant to corrosion by high-temperature water. It has been found in work at low temperatures that alloys containing even slight additions of zirconium to the uranium (<20 w/o) exhibit better corrosion resistance than does pure uranium.^(1, 2) Nevertheless, the corrosion of these high-uranium alloys can be serious, especially at water temperatures at or above 600 F. Consequently, a cladding is needed, not only to retain fission products, but also to provide additional protection against corrosion. The possibility exists, however, that a defect can develop in the cladding. The core is then in contact with the water, and the volume expansion resulting from oxidation of the uranium can enlarge the defect. In fact, if the mechanical strength of the bond between the cladding and core is weak, progressive oxidation may well result in complete destruction of the fuel element, even though the initial defect is but a small pinhole. Factors which might affect this failure are the strength properties of the cladding material, the bond strength between the core and cladding, the operating

(1) References at end.

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temperature, the geometrical shape of the fuel element, the impurities in the water, and the corrosion rate of the core.

A major portion of this investigation was the development of a windowed autoclave with which this rupturing phenomenon could be studied. This device was fitted with a time-lapse motion-picture camera to permit the observation of the physical changes in the specimen and the evolution of hydrogen as bubbles during the corrosion process. A recording pressure gage provided quantitative data on hydrogen-evolution rates. Information obtained in this fashion, together with geometrical considerations, was used to calculate corrosion rates.

Initial experiments were concentrated on finding the effects on the core-corrosion rate of (1) water temperature, (2) percentage of zirconium in the core alloy, and (3) the presence or absence of cladding.

APPARATUS

In order to study the reaction of defected specimens in high-temperature water, the autoclave system was designed to withstand temperatures up to 700 F and pressures to 3000 psi. The test vessel is the windowed autoclave pictured in Figure 1. Two Herculite glass windows are mounted at the ends of legs extending downward from the main body of the autoclave. Cooling the legs maintains the water inside them at a low enough temperature to avoid etching of the glass, and the useful life of the windows is thus extended indefinitely. Since the cooler, more dense water is in the lowest part of the autoclave, there is no tendency for convection currents to disrupt the optical path.

Water is raised to the test temperature in a separate preheat autoclave, shown in Figure 2. Therefore, no reacting of the defected specimen takes place until this elevated-temperature water is allowed to suddenly engulf the preheated test specimen. It is felt that this more closely simulates the effect of an actual defect occurring in a fuel element during reactor operation.

An arrangement of mirrors, a light source, and a digital timer, along with a time-lapse camera system, have been incorporated to record the visible change in the specimen during a test. The optical system, shown in Figure 3, is adjusted so that a picture is taken simultaneously of the specimen and the timer. Thus, each frame can be identified by the elapsed time from initial contact of the specimen with the elevated-temperature water. The remaining equipment in the system includes a pressure recorder for obtaining data on the total system pressure versus

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ID of legs 1"

ID of body 2-1/2"

Distance, specimen
to window $\approx 12"$

Volume in legs..... 200 cc

Volume in body
and tubing..... 430 cc

Total volume in
test-vessel system..... 630 cc

FIGURE 1. CROSS SECTION OF WINDOWED AUTOCLAVE

FIGURE 2. WINDOWED AUTOCLAVE SYSTEM

FIGURE 3. PHOTOGRAPHING AND OBSERVATION SYSTEM

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time, and valving and tubing to facilitate the initial charging with water and subsequent transfer of hot water from the preheat to the windowed autoclave.

SPECIMEN DESCRIPTION

Two shapes of specimens were chosen for this series of tests, a pin shape and a flat disk. These were chosen both for their ease of fabrication and for their geometrical similarity to two common classes of fuel elements, rods and plates.

The pin-type specimens, depicted in Figure 4, were fabricated with uranium-0, 5, 10, 15, and 20 w/o zirconium alloy cores. Although some specimens of each core alloy were fabricated with an attempt to produce a metallurgical bond, it was found after running several of them in the autoclave tests that unless the bond was exceptionally strong, separation occurred at the bond line adjacent to the reacted region. This made the evaluation of the instantaneous exposed core area, required for the corrosion-rate calculation, extremely difficult.

The coin-shaped specimen, illustrated in Figure 4, was chosen for investigating the effect of bonding on the corrosion rate, since this shape proved easier to handle analytically than the bonded pin shape. The specimens were fabricated by die pressing the loosely assembled pieces under vacuum at high temperature, and maintaining the pressure for several hours to effect bonding along all interfaces.

DATA AND RESULTS

Data taken during a test include a film record, a pressure-time curve, and a temperature-time record. Figure 5 shows a sequence of frames selected from the film record of the reaction of a defected, clad, pin-type specimen containing a pure-uranium core which is being subjected to 600 F water. The 10-mil defect drilled through the zirconium cladding can be seen near the center of the specimen in the first few frames. The timer indicates that these nine frames span the time interval from 0.50 to 40.85 min. As can be estimated from the progress of the swelling, the reaction of the core at this temperature was quite rapid, and the cladding developed a split after less than 15 min. In this particular test, after only 40 min, the rupture had progressed to the point that oxide debris was falling onto the windows; by 50 min, the debris had completely obscured the view.

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a. Pin Type

b. Coin Shape

FIGURE 4. SPECIMEN CONFIGURATIONS

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NOTE: Far right dial on digital timer indicates tenths of minute.

FIGURE 5. REPRESENTATIVE REPRODUCTIONS FROM FILM OF A TEST

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In the film records of a number of tests, however, it was possible to continue to see the specimen clearly until the entire core had been oxidized. When this happened, two independent methods of computing the corrosion rates were available. One was based on the total time required for the known volume of the core to be reacted, which could be obtained by studying the films and noting the instant at which the last bubble of hydrogen was evolved. The other made use of the rate of hydrogen evolution, as evidenced by the pressure and temperature records. In general, these two methods agreed within 20 per cent, which is the estimated range of experimental error at best (based on the accuracy of the contributing data).

To determine hydrogen-evolution rates, it was necessary to subtract the steam pressure from the total system pressure and to correct for hydrogen solubility in the water. Steam pressures were determined from steam tables as vapor pressures corresponding to the measured water temperatures. Figure 6 shows a typical plot of total pressure, steam pressure, and hydrogen pressure. The hydrogen-evolution rate can be computed from this, with the aid of the perfect gas laws, since the gas volume and temperature are known. On the basis that the reacted uranium forms UO_2 (which has been verified by analysis of the debris), the hydrogen-evolution rate can be converted to moles of uranium oxidized per unit time. This is simply one-half the mole of hydrogen liberated per unit time.

Calculation of the corrosion rate per unit of exposed surface area requires a knowledge of the functional relationship between the instantaneous core area exposed to the water and the corroded volume. The analysis is presented in the Appendix, along with graphs of the geometrical relationships for the particular specimen shapes used in this study. As is generally done, the assumption is made that attack proceeds at a uniform rate in the direction perpendicular to the surface being corroded.

Table 1 gives average values of core-corrosion rates for various test and specimen conditions. To check the validity of the assumption of a constant corrosion rate, the values were calculated for several different intervals of time [Equation (A-4), Appendix] in each case. Although some rates appeared to increase slowly while others seemed to decrease as the reaction progressed, the variation about the mean was in no case larger than 20 per cent, and no correlation could be obtained with test conditions.

As will be noted in Table 1, the water temperature was rarely exactly 600 F. Factors determining the water temperature were too numerous to permit exact control. Thus, the uranium-0, 5, and 10 w/o zirconium alloys are compared graphically in Figure 7 as a function of temperature. Since no other experimental data were available for comparison purposes in this temperature region, the lower temperature values of Mollison, English, and Nelson⁽³⁾ were extrapolated to the 600 F range.

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FIGURE 6. TYPICAL PLOT, PRESSURES VERSUS TIME

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TABLE 1. AVERAGE CORROSION RATES OF URANIUM AND URANIUM-ZIRCONIUM ALLOYS BY PRESSURIZED HOT WATER

Nominal Zirconium Content (Balance Uranium), w/o	Specimen Shape	Cladding Condition	Average Water Temperature, F	Average Corrosion Rate, mg/(cm ²)(hr)
0	Pin	Unclad	587	6,260
	Pin	Unbonded	582	4,910
	Pin	Unbonded	600	5,330(a)
	Pin	Unbonded	603	3,190
	Pin	Unbonded	605	3,800
	Pin	Unbonded	610	4,850
5	Pin	Unclad	587	3,150
	Pin	Unbonded	600	4,860
	Pin	Unbonded	612	6,300
	Coin	Bonded	595	2,120
	Coin	Bonded	600	4,440
10	Pin	Unclad	595	2,780
	Pin	Unclad	602	2,310
	Pin	Unbonded	570	2,330
	Pin	Unbonded	590	13,000
15	Pin	Unbonded	604	165(a)
20	Pin	Unbonded	610	194(a)

(a) Corrosion rates calculated from time required for complete oxidation of core, as ascertained from cessation of hydrogen bubbling on film record. All others computed from pressure records.

FIGURE 7. AVERAGE CORROSION RATES OF URANIUM AND URANIUM-ZIRCONIUM ALLOYS VERSUS THE RECIPROCAL OF TEMPERATURE

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This gave the straight line in Figure 7 which, though the validity of such extrapolation may be questioned, serves as an order-of-magnitude basis of comparison for the test points.

DISCUSSION AND CONCLUSIONS

The principal purpose of this investigation, as stated earlier, has been the development of a research tool. Toward this end, the relatively small number of tests run thus far have provided adequate evidence of both the flexibility and limitations of the windowed autoclave.

Data obtainable from the time-lapse photographs, although more qualitative than quantitative in nature, are of some value in this particular type of test because the swelling and rupture of the cladding resulting from the core reaction is clearly visible, and serves to confirm the rapidity with which low-zirconium alloys of uranium are oxidized in high-temperature water. In addition, by projecting the time-lapse film record of a test at the normal speed of 16 frames per sec, it is possible to observe the manner in which a particular cladding configuration fails.

Since the swelling produced in the cladding is a direct result of the uranium in the core being converted to the less dense UO_2 , it was felt that a more quantitative evaluation of the influence of various factors on specimen rupture could be made by means of the core-corrosion rate. For this reason, the method of determining the core-corrosion rate from the partial pressure of hydrogen was developed.

Although the results obtained from these tests have an accuracy no better than 20 per cent (based on the accuracy with which the pressures, etc., can be measured), some conclusions may be drawn from the data based on order-of-magnitude comparisons. By referring again to the graphical representation of data (Figure 7), one observes that clad specimens react at nearly the same rate as unclad ones, and zirconium additions up to 10 w/o provide only slight protection to the uranium core. On the other hand, the corrosion rates of the 15 and 20 w/o zirconium alloys were found to be an order of magnitude smaller than those of the pure uranium or the uranium-10 w/o zirconium alloy.

The large dispersion of the experimental points in the unalloyed uranium and uranium-10 w/o zirconium specimens overshadows any noticeable temperature effect; however, the data for the 5 w/o zirconium alloy show a definite increase in corrosion rate at higher temperatures. This strong temperature dependence has been substantiated by other

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Poor Bond
5 Hr of Exposure

Well Bonded
10 Hr of Exposure

FIGURE 8. RUPTURE OF BONDED COIN SPECIMEN OF URANIUM-5 w/o ZIRCONIUM TESTED IN 595-600 F WATER

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investigators and explains the sizable errors that may arise from difficulties in determining specimen temperature precisely.

The discrepancy between the experimental points of the pure uranium specimens and the line obtained from the data of Reference (3) may be due not only to the large experimental error involved but to the doubtful validity of extrapolating from data at considerably lower temperatures into this range.

Although the corrosion rate is apparently unaffected by cladding or bonding a high-uranium-alloy core with a protective covering of zirconium, the rate of rupture is decreased as the degree of the bonding is increased. This is to be expected, since the core surface exposed through a defect in a bonded element will be considerably less than in one with no bond. An example of this may be seen in Figure 8. It will be noted that the rupture is less severe in the specimen with the stronger bond, and in fact, after twice the exposure, a section of the well-bonded specimen core was still unreacted.

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- (3) Mollison, W. A., English, G. C., Nelson, F., "Corrosion of Tuballoy in Distilled Water", CT-3055 (June 23, 1945).

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APPENDIX

GEOMETRICAL CONSIDERATIONS IN CORROSION-RATE CALCULATIONS

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APPENDIX

GEOMETRICAL CONSIDERATIONS IN CORROSION-RATE CALCULATIONS

A corrosion rate is one of the commonly calculated quantities used for comparing the resistance of materials to the corroding action of a particular medium. It is the rate of reaction per unit of macroscopic surface area exposed to the corrodent, and is ordinarily expressed as the mass of material reacted per unit area per unit of time.

That is,

$$k = \frac{1}{A} \frac{dM}{dt}, \quad (A-1)$$

where

k = corrosion rate,

A = exposed area,

$\frac{dM}{dt}$ = time rate of mass reaction.

Using the relation:

$$V = M\rho, \quad (A-2)$$

where

ρ = mass density of parent material, and

V = volume of material reacted,

Equation (A-1) may be expressed as:

$$k = \frac{\rho}{A} \frac{dV}{dt}. \quad (A-3)$$

If the area exposed is a function of the volume corroded: $A = f(V)$ and the reaction rate, k , is a constant with respect to time, the equation may be rearranged and integrated:

$$k = \frac{\rho}{(t_2 - t_1)} \int_{V_1}^{V_2} \frac{dV}{f(V)}, = \frac{\rho}{(t_2 - t_1)} R, \quad (A-4)$$

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where $(t_2 - t_1)$ is the time interval during which the corroded volume increases from V_1 to V_2 ,

and R represents the $\frac{\text{volume}}{\text{area}}$ integral.

If we let $t_1 = 0$ when $V_1 = 0$, Equation (A-4) becomes:

$$k = \frac{\rho}{t_2} R_0, \text{ where } R_0 = \int_0^{V_2} \frac{dV}{f(V)} \quad (A-5)$$

In order to apply this formula to a particular corrosion-rate calculation, the specific geometry involved must be known, i. e., $A = f(V)$. An example might be a cube with side length s , completely submerged in a corrosive fluid.

Let r be a depth of corrosion.

Thus:

(a) $V = s^3 - (s - 2r)^3$, volume corroded

(b) $A = 6(s - 2r)^2$, instantaneous area exposed to fluid.

Solving (a) for r in terms of V :

$$r = \frac{s - (s^3 - V)^{1/3}}{2}$$

and substituting this value for r in (b) gives:

$$A = f(V) = 6(s^3 - V)^{2/3}.$$

Then, in the case of a cube, Equation (A-5) becomes:

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$$k = \frac{\rho}{t_2} \int_0^{V_2} \frac{(s^3 - V)^{-2/3}}{6} dV.$$

Integrating yields:

$$k = \frac{\rho}{t_2} \left[\frac{(s^3 - V)^{1/3}}{(-2)} \right]_0^{V_2}.$$

And finally:

$$k = \frac{\rho}{2t_2} \left[s - (s^3 - V_2)^{1/3} \right],$$

where:

t_2 = length of time reaction has been going on

V_2 = volume reacted after time t_2 .

The corrosion rate of a cube may now be calculated if one knows the density (ρ) of the material and the volume (V_2) that is reacted in elapsed time (t_2). This reacted volume might in turn be calculated from: (1) a weight change, (2) a change in dimensions, (3) the quantity of reaction products formed, or (4) the amount of a side product formed in the reaction.

In a similar manner, it is possible to calculate a corrosion rate for any case in which the geometry is known and the exposed area can be expressed as a particular function of the reacted volume. For illustrative purposes, this relationship is presented for four geometries which might be encountered in reactor fuel elements. It is assumed that the corrosion of any exposed surface proceeds perpendicular to that surface at a uniform rate. Thus, when access to the core is through a pinhole in the bonded cladding, the corrosion would proceed spherically from that point. An additional assumption is made that the corroding medium has free access to the surface, with no masking by corrosion products. The sample cases are as follows:

- Case I. An unbonded or unclad pin with protected ends, in which case the corrodent has access initially to the entire lateral surface but not the ends.
- Case II. A completely bonded pin, in which initial contact of the corrodent occurs at a localized point on the lateral surface.

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Case III. A pin with a bonded lateral surface and an unbonded end, in which the corrodent has free access to this end.

Case IV. A completely bonded cylinder, in which the corrodent contacts the core initially at a point located at the center of one of the ends.

These four cases are presented graphically in Figures A-1 through A-4, in which the instantaneous corroded volume and exposed area are plotted against a common parameter, r , the instantaneous depth of penetration of the corrodent. The mathematical steps for obtaining the final relationships between corrosion rate and reacted volume are not included; instead, the results of the integration for the four pin shapes are presented graphically in Figure A-5 and A-6, and, for a bonded flat-disk shape, in Figure A-7.

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FIGURE A-1. VOLUME OF MATERIAL REACTED AND EXPOSED SURFACE AREA AS FUNCTIONS OF DEPTH OF CORROSION

Case I: Unbonded or unclad pin with protected ends; entire lateral surface exposed to corrodent.

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$$V = 4 \int_0^r \int_0^{\pi/2} \int_0^{\cos^{-1}\left(r \frac{\sin \theta}{2a}\right)} r^2 \sin \theta \, d\theta \, d\phi \, dr, \text{ for } r \leq 2a.$$

$$V = 4 \int_{2a}^r \int_0^{\sin^{-1}\left(\frac{2a}{r}\right)} \int_0^{\cos^{-1}\left(r \frac{\sin \theta}{2a}\right)} r^2 \sin \theta \, d\theta \, d\phi \, dr + 4 \int_0^{2a} \int_0^{\pi/2} \int_0^{\cos^{-1}\left(r \frac{\sin \theta}{2a}\right)} r^2 \sin \theta \, d\theta \, d\phi \, dr, \text{ for } r > 2a.$$

FIGURE A-2. VOLUME OF MATERIAL REACTED AND EXPOSED SURFACE AREA AS FUNCTIONS OF DEPTH OF CORROSION

Case II: Bonded pin, contact of corrodent at localized area on lateral surface.

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Case III: Pin with bonded lateral surface; corrodent contacts unbonded end.

FIGURE A-4. VOLUME OF MATERIAL REACTED AND EXPOSED SURFACE AREA AS FUNCTIONS OF DEPTH OF CORROSION

Case IV: Bonded pin, corrosent initially contacts localized area c and.

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FIGURE A-5. VOLUME/AREA INTEGRAL AS A FUNCTION OF REACTED VOLUME FOR AN UNBONDED OR UNCLAD FUEL PIN WITH PROTECTED ENDS AND ENTIRE LATERAL SURFACE EXPOSED TO CORRODENT (CASE I)

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FIGURE A-6. VOLUME/AREA INTEGRAL AS A FUNCTION OF REACTED VOLUME FOR FUEL PINS

- Case II: Bonded side, bonded end, hole in side.
- Case III: Bonded side, unbonded end, hole in end.
- Case IV: Bonded side, bonded end, hole in end.

FIGURE A-7. VOLUME/AREA INTEGRAL AS A FUNCTION OF REACTED VOLUME FOR COMPLETELY BONDED COIN-SHAPED SPECIMEN WITH $R = 8h$
Pinhole in center of one face.

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